Separation of Volatile Organics (Benzene and Toluene) from water using PDMS Membrane
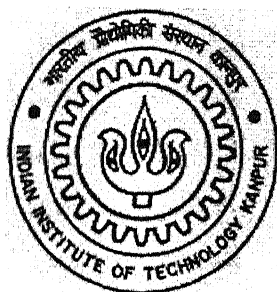
A thesis submitted
in partial fulfillment of the requirements
for the degree of
Master of Technology

By

Prince George

to the

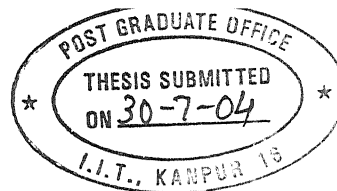## DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

JULY, 2004
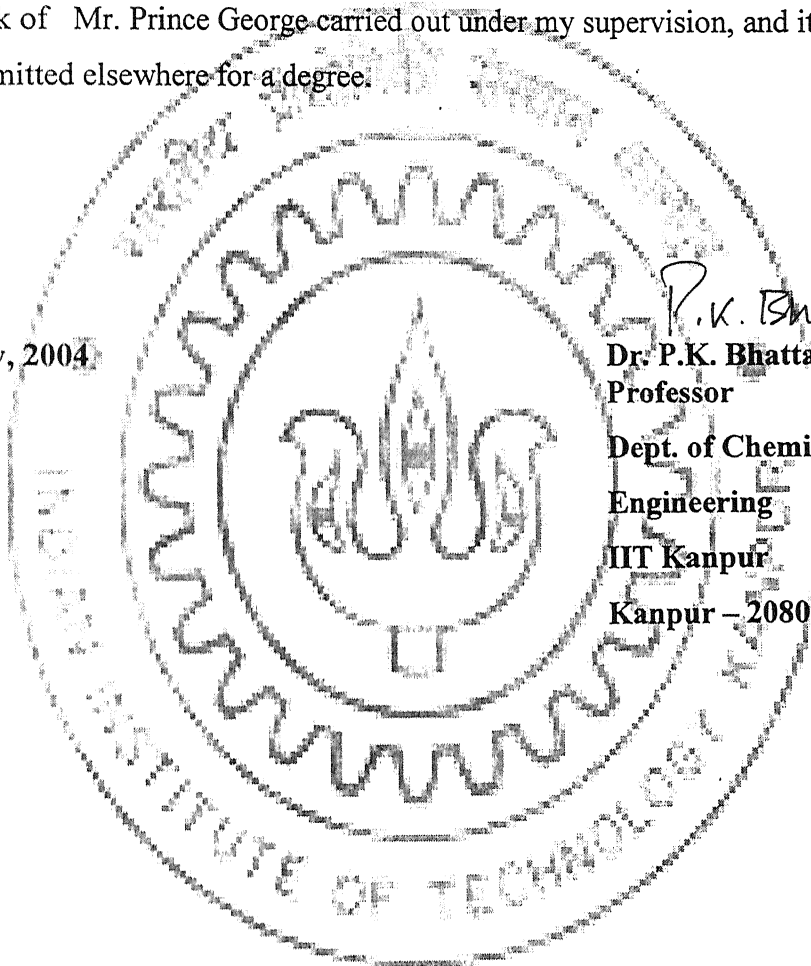
CERTIFICATE

This is to certify that the thesis entitled "**Separation of Volatile Organics (Benzene and Toluene) from water using PDMS Membrane**" is the original work of Mr. Prince George carried out under my supervision, and it has not been submitted elsewhere for a degree.

30th July, 2004

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Dedicated

To

MY PARENTS

&

SISTER

Abstract

Separation of benzene- toluene- water mixture was carried out by pervaporation process using PERVAP Teflon coated organophilic PDMS membrane for different feed concentrations of total organics. The membrane showed good selectivity for organics. It was found that the membrane showed more affinity towards benzene than toluene. The inverse relationship between selectivity and flux was obtained when experiments were carried out at same total organic concentrations, but at differing compositions of benzene and toluene. With increase in benzene concentration in the feed it was found that the membrane showed greater selectivity and a maximum was reached, however it was at the expense of total flux. The selectivity of the membrane showed a maximum when both benzene and toluene were present in the feed, compared to a binary system of either benzene or toluene in water. Pervaporation studies at different total organic concentrations with varied composition of benzene and toluene were compared. It was found that there is a right shift for maximum values of total organic selectivity towards higher benzene concentration with increase in total organic concentration in feed. It was also found that benzene separation factor increased with increase in total organic load on the membrane at equal amounts of benzene and toluene in the feed. A model was developed for predicting the values of flux and concentrations for equal amount of benzene and toluene in feed. The values of flux and selectivity as predicted by the model were well matched with the experimentally obtained values.

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I cannot end without thinking of my family, on whose constant love and blessings, I have always relied upon and I hope to continue, in my small way, like this.

Prince George

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NOMENCLATURE

a_i activity of component i

a   a constant

C   volumetric concentration (m^3/m^3)

c   molar concentration ($kmol/m^3$)

D   diffusivity (m^2/s)

$\tilde{D}_i$ mean diffusion coefficient (m^2/s)

$D_{i,K}$ Knudsen diffusivity (m^2/s)

H   Henry's law constant (mmHg)

J   volumetric flux (m^3/m^2s)

K_i Henry's law partition coefficient

K_L molar concentration based mass transfer coefficient (m/s)

K_x mole fraction based overall mass transfer coefficient ($kmol/m^2$ s)

$k_{i,v}$ mass transfer coefficients of vapor components

k_L molar concentration based mass transfer coefficient (m/s)

k_m mass transfer coefficient in the membrane ($kmol/m^2 mmHg.s$)

k_x mole fraction based mass transfer coefficient ($kmol/m^2$ s)

L_i Top layer permeability

l thickness of membrane (m)

M_i molecular weight of i

m_i mobility

N   molar flux ($kmol/m^2s$)

P	Permeability (m kmol/m^2.mmHg.s)
P$_3$	Permeate pressure (mm Hg)
$\overline{P}$	overall average permeability (m kmol/m^2.mmHg.s)
p	partial pressures
p^o	saturation pressure (mmHg)
$\overline{p}$	average permeability in the membrane (m kmol/m^2.mmHg.s)
R	universal gas constant (J/kmol K)
R$_i$	Enhancement factor
r	pore radius (m)
T	absolute temperature (K)
t	time (s)
V	molar volume (m^3/kmol)
v$_p$	velocity of the fluid (m/s)
x	liquid phase mole fraction
y	vapour phase mole fraction
z	axial coordinate

GREEK SYMBOLS

α	Selectivity
α_{ij}	Coupling Factor
β	Separation Factor
β_{ij}	Effective Coupling coefficient

ε   Porosity

γ   activity coefficient

ρ   molar density (kmols/m^3)

μ   chemical potential

δ   membrane thickness (m)

φ   Swelling Factor

ψ_i Partition coefficient of component i

τ   Tortuisity

SUBSCRIPTS

1   solution side

2   evaporation surface

3   bulk vapour

A   organics

B   water

b   bulk

evap   evaporation

i   organic component

M   Membrane

m   inside membrane

mem   membrane

o   reference state

p   permeate

ix

pv pervaporation

s surface

w water

SUPERSCRIPTS

act actual

F feed side

m a constant

n a constant

P permeate side

ABBREVIATION

FID Flame Ionization Detector

GC Gas Chrotograph

PV Pervaporation

PDMS Poly-Dimethyl Siloxane

PVA Poly-vinyl Alcohol

VOC Volatile Organic Compound

Re Reynolds Number

Sc Schimidt Number

Sh Sheerwood Number

CHAPTER 1
INTRODUCTION

Water contaminated with VOCs is encountered in several chemical industries, groundwater and site remediation applications. Conventional technologies such as air stripping and adsorption with activated carbon do not always provide a complete and economic solution for some of these waste water applications. In recent years, pervaporation [1, 13] using hydrophobic membrane has been observed to be promising and potentially suitable remediation method for such applications. Further, VOCs (aromatic hydrocarbons and chlorinated hydrocarbons used as washing solvents in chemical industry) cause soil pollution. Such pollution contaminates subterranean water and consequently water in rivers and ponds. Drinking water sources are often dependent on such contaminated water. VOCs are known to be chemical materials disturbing internal secretion (environmental hormones) which are potentially dangerous to human life. Pervaporation is a promising membrane technique for the separation of VOCs/water mixtures [15, 1, 16, 17 and 18].

Pervaporation is a novel membrane separation technique for the removal of volatile organic compounds (VOCs) from aqueous medium, dehydration of organic solvents, close boiling mixtures and azeotropes. Pervaporation has also emerged as a good choice for separation of heat sensitive products. Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. The conventional method of distillation is best used under the conditions of existence of differing boiling points of the components. For azeotropic mixtures, a third component is used to carry out the separation and the recovery of the third component increases energy consumption making the overall process expensive. Likewise, air stripping is limited to the removal of compounds that significantly partition to air over water. In addition to the above limitations, unless the off-gas is treated, air stripping merely turns a water pollution problem into an air pollution problem. With all these comparative perspectives, pervaporation process seems to be significantly promising. Further, preliminary calculations show that the capital cost of the plant fall in the range $ 2–5/gal of feed water per day with an operating cost of $ 2–10/1,000 gal of feed water treated [1].

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Pervaporation is a separation process in which a liquid mixture is in direct contact with one side of a membrane and the permeated product (the 'pervaporate') is removed in the vapour state from the other side. The component in the liquid stream if gets sorbed into the membrane, it permeates through the non-porous membrane. The mass flux is affected by maintaining the downstream pressure much lower than the saturation pressure at the prevailing condition (such a low pressure can be achieved either employing a carrier gas or using a vacuum pump at the downstream side). The membrane acts as a thin solvent layer and the permeation gets mainly governed by the preferential solvation. As a result, the liquid-vapour equilibrium is greatly perturbed. The permeating molecule finally changes into its vapour as and when its meets pressure lower than its corresponding condition either within the membrane or just outside the membrane at the downstream side. The size of the molecules that need to be separated selectively permeate through a nonporous membrane may be in the same order of magnitude. In a pervaporation membrane process, it is desirable to have a polymeric film having properties of high permeation combined with good selectivity [30]. In order to obtain good permeation rates and a high degree of separation for a liquid mixture, it is desirable to choose a proper membrane under optimum operating conditions. A schematic diagram of liquid permeation through a dense membrane in a pervaporation process is shown in Fig 1.1.

In a pervaporation membrane process, it is desirable to have a polymeric film having properties of high permeation combined with good selectivity [30]. In order to obtain good permeation rates and a high degree of separation for a liquid mixture, it is essential to choose a proper membrane as well as optimum operating conditions. Further, the mass transport of the permeating molecule through the pore-free permselective film may involve three successive steps:

a) Sorption of the permeating molecule at the interface of the solution feed and the membrane,

b) Diffusion of the permeating molecule across the membrane due to its concentration gradient, and

c) Desorption of the permeating molecule into its vapor phase at the downstream side of the membrane.

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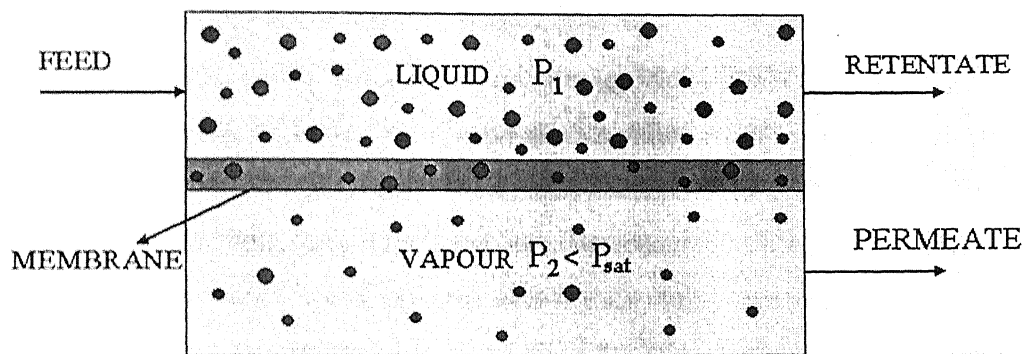
Figure 1.1: Liquid permeation through a dense membrane in vapour form

This multi-step process is evidently much more complex and it is easily understandable that the composition of the pervaporate may widely differ from that of the mixed vapour evolved after the establishment of free liquid-vapour equilibrium. The use of an appropriate membrane generally makes it possible to efficiently separate a number of binary azeotropic mixtures.

PDMS (poly-dimethyl-siloxane) membranes have been studied as VOC-permselective membranes; because they have a high permselectivity and permeability for organic chemicals in water [19-22]. The high VOCs - permselectivity of the PDMS membrane is attributable to its stronger affinity for VOCs than for water. Further, VOCs display high diffusivity through PDMS polymer due to its low T_g. However, PDMS membrane suffers with weak mechanical strength [14].

The effluents from petrochemical industry contain VOCs in ample amount. Petroleum hydrocarbons, and other volatile organic compounds (VOCs) which are found to contaminate groundwater and soils, are usually treated by pump-and-treat methods which are time-consuming, expensive and not significantly effective. Pervaporation effectively removes these hydrocarbons and VOCs from contaminated soil and groundwater (with or without using surfactants) and concentrating them by at least a thousand-fold, for economical disposal or recycle/reuse using specially designed hydrophobic membranes.

Studies on the effect of operating parameters such as feed concentration, down stream pressure, temperature, etc on the performance of the pervaporation process for the removal of VOCs assumes great significance. The separation of binary mixtures of VOC-Water has been studied [] in great details. However, effluents from industries such as petrochemical industries contain multi-component VOCs. Studies with such multi-component feed mixtures are rare and mostly confined to certain case specific purposes. The present work, therefore, was undertaken to study separation of ternary mixture of VOCs – Water. Two important VOCs present in waste water are benzene and toluene. They occupy the first two positions of the homologous series and hence have similar properties. The separation between them is difficult by conventional processes; particularly when they are present in ppm concentrations. Separation of individual components like benzene and toluene from water, as binary mixtures, has been earlier

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reported [22, 47]. But to our knowledge, there is no report of simultaneous separation of benzene and toluene, present in ppm concentration in water which may then become an interesting approach. Accordingly, it was decided to study pevaporation of benzene-toluene in aqueous medium using organophilic PDMS membrane. Further, it would be interesting to observe and investigate the performance of PV under different compositions of the feed mixture (however, in and around the solubility limits of benzene and toluene in water) at fixed downstream pressure and feed temperature.

Based on above discussion and understanding of the importance of the earlier work, following broad objectives are laid down for the present work:

i)   To observe the influence of concentration of the VOCs on pervaporation process using commercial PERVAP Teflon coated organophilic PDMS membrane.

ii)   To observe separation (in terms of selectivity and separation factor) of two VOCs (benzene and toluene) as compared to single VOC- water systems.

iii)   To access the performance of commercially available organophilic PDMS membranes with regard to ternary VOCs-water system.

iv)   To study the effect of coupling during multi-component VOCs separation.

Separation processes play an important role in the chemical industries for purifying raw materials, recovering product streams of desired purity and preventing pollution through treatment of waste streams released to the environment. It was estimated that around 30-70% of the capital cost of the chemical industry is accounted by separation processes [2]. Pervaporation is a novel membrane separation technique for the removal of Volatile Organic Compounds (VOCs) from aqueous medium, dehydration of organic solvents, close boiling mixtures and azeotropes. Pervaporation has also emerged as a good choice for separation heat sensitive products. Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. The conventional methods which are in usage for the separation of liquid mixtures are distillation, solvent extraction, adsorption and air stripping. The distillation process is best used when the boiling points of the components of the mixture are not close, and thereby the separation occurs based on the difference in boiling points. However, for the close boiling mixtures and the mixtures at azeotropic composition, the vapor pressures of the components are close and thereby their separation is not possible by ordinary distillation. For close boiling mixtures, extractive distillation is used, where a third component is mixed and thereby the separation is carried out; and for the azeotropic mixtures, a third component, called entrainer, is used to carry out the separation. Therefore, the third component has to be recovered by another distillation process which increases the energy consumption and make the overall process expensive. In solvent extraction, one of the components of the mixture is more soluble in the extractive solvent and thereby the separation is carried out. However, recovery of the solvent makes the process expensive. In adsorption process, the recovery of adsorbent adds to the cost of the process. Air stripping is limited to the removal of compounds that significantly partition to air over water. In addition to the above limitations, unless the off-gas is treated, air stripping merely turns a water pollution problem into an air pollution problem. With all these comparative perspectives, pervaporation process seems to be significantly promising. The fouling is minimal because air is not added to water and there is no need

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to use the third component as in solvent extraction or azeotropic distillation. Further, additional operations, like recovery/regeneration are avoided which adds to the value of the product obtained from pervaporation process. Thus Pervaporation appears to be an economically viable method of removing non-polar solvents from dilute aqueous streams.

2.1 Pervaporation Process

The origins of pervaporation can be traced to the 19th century, but the first systematic studies were done in the late 1950s [3]. The phenomenon of pervaporation was first observed by Kober [4] for his experiments on evaporation of water placed in a collodion (cellulose nitrate) bag into atmospheric air. Before to this, in 1906 Kahlenberg [5] reported some qualitative observations concerning the selective transport of hydrocarbon/alcohol mixtures through a thin rubber sheet. In 1935, Farber [6] recognized the usefulness of pervaporation for separation and concentration. However, Heisler et al. [7] reported the first quantitative work for the separation of alcohol/water using cellulose film by pervaporation. Binning and co-workers [8, 9] carried out pervaporation of different mixtures and highlighted the potential application of pervaporation. A first commercial application of pervaporation, installed in Brazil, was reported in 1982 [10] for the separation of alcohol-water mixtures using G.F.T. (Gesellschaft für Trenntechnik, Homburg/Saar, F.R.G) membrane. Meanwhile, development of new membranes, experimental investigations, fundamental understandings, theoretical models, and module designs are in progress [11, 12].

Pervaporation is a separation process in which a liquid mixture is in direct contact with one side of a membrane and the permeated product (the 'pervaporate'), is removed in the vapour state from the other side. The components in the liquid stream get sorbed into the membrane and permeate through the membrane. The permeating molecule finally changes into its vapour as and when its meets pressure lower than its corresponding condition either within the membrane or just outside the membrane at the downstream side. The sizes of the molecules that need to be separated are in the same order of magnitude. Thus, nonporous membranes are employed and porous membranes do not function effectively. Further, the mass flux may be affected by maintaining the downstream pressure much lower than the saturation pressure at the prevailing condition.

Such a low pressure can be achieved either employing a carrier gas or using a vacuum pump at the downstream side. The membrane acts as a thin solvent layer and the pervaporate composition is mainly governed by the preferential solvation of the polymeric barrier material. As a result, the liquid-vapour equilibrium is greatly perturbed.

2.2 Pervaporation characteristics

i. *Molecular or mass flux*: - It is the amount of a component permeated per unit area per unit time for a given membrane.

ii. *Permselectivity*: - The performance of a given membrane can be expressed in terms of this parameter.

iii. *Permeability coefficient*: - The flux across the membrane is related to driving force using this term.

2.3 Pervaporation membranes

Selection of an appropriate membrane material is facilitated by recognizing the fact that membrane permeation is governed by both the chemical nature of the membrane material and the physical structure of the membrane. In reality, industrial suppliers for pervaporation membranes are extremely scarce world wide [42]. The chemical structure of the membrane active layer is either very simple and almost identical for all the existing suppliers (as way of examples: polyvinyl alcohol PVA or polydimethylsiloxane PDMS) or more complex and very specific to given mixtures, exclusively organic mixtures in particular, and therefore, often confidential. As it is widely accepted in this field, three different types of membranes can be distinguished according to their own specificity:

1) Hydrophilic membranes
2) Organophilic membranes
3) Organoselective membranes

2.3.1 Hydrophilic membranes

The hydrophilic membranes were the first ones to have found an industrial application for the organic solvent dehydration by PV and they keep their dominance still in the industry today. These types of membranes are typically made of polymers with

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glass transition temperature above room temperature. Owing to their hydrophilic character, these membranes enable to extract water fluxes and selectivity depending upon the chemical structure of the active layer and upon its way of cross linking. Majority of PERVAP 22xx series membranes belong to this class.

2.3.2 Organophilic membranes

Organophilic membranes are used to recover organic solutes from aqueous or gaseous effluents. There is a great predominance of a very few chemical structures (PDMS and related polymeric materials) amongst the commercial organophilic membranes. PERVAP 1060/1070 belong to this category.

2.3.3 Organoselective membranes

The organoselective membranes indeed considerably extend the potential of PV by addressing the difficult problem of separating purely organic mixtures. New developments in this field have already shown that these membranes could be very specific answer to key separation problems especially in the petrochemical industry. Despite a very intense research activity, only two cases of industrial applications have so far been reported (by Sulzer Chemtech®).

2.4 Research on VOCs removal by PV

The efficiency of PV separation is determined by properties of the target substance and of the membrane as well as by operation variables like feed temperature, permeate pressure, feed concentration, and feed liquid velocity. Studies of PV performance and related issues on VOCs can be grouped into three categories:

• *PV membrane*: Membranes used for VOC separation from water are mostly non-porous hydrophobic ones in a layered composite or dense form. The aim is to test, evaluate, and/or improve the performance of the PV membrane in terms of selectivity, flux, mechanical strength, and optimization of casting techniques and ingredients.

• *Specific VOCs*: Closely related with research on membranes is the study of behavior of different VOCs and interaction between the individual organic compounds as well as between the VOCs and the membranes. For example, industrial wastewaters are multi-component systems, and often behave differently during PV as compared to a similar simple binary system.

• *Operating variables*: The PV process for separating VOCs from water is influenced by process variables. The evaluation and understanding of these variables such as feed temperature, feed concentration, vacuum, and feed velocity are always important in achieving effective separation. Generally, water and solute flux both increase with an increase in either feed temperature or feed concentration for a fixed permeate pressure. However, the extent of water and solute flux variation under these circumstances, as well as the corresponding separation factor will depend on properties of the organic compound and its interaction with the membrane and therefore need to be examined individually [23].

2.5 PV Membranes used for VOC Removal

The membrane is the heart of PV. The first criteria for judging a membrane is whether it separates the target solute from water. The PV membrane can be considered as a dense homogenous medium in which diffusion of species takes place in the free volume that is present between the macromolecular chains of the polymeric membrane material. VOCs encountered in an environmental remediation operation usually have concentrations in the range of 1–500 ppm (mg/l) [23]. As a general rule, the membranes used for separating VOCs from dilute solutions are mostly hydrophobic materials [23]. Although the partitioning behavior of the VOCs into the membrane will vary, the partitioning behavior still favors VOC sorption into the membrane. Hydrophobic materials are preferred in this application because separating a small amount of organic compounds from the mixture is easier and consumes much less energy than separating water from aqueous solutions. PV membranes used for VOC removal from water can be

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either symmetric or composite with a selective layer of 1–200 μm mounted on one or two layers of porous supporting material.

The most commonly used hydrophobic membrane for VOC removal consists of a selective layer of polydimethylsiloxane (PDMS), also known as silicone rubber, which has an alternating ---O---Si---O--- unit structure and has very good stability in operation This membrane has very good processing properties and is suitable for manufacturing ultrathin composite membranes. The selectivity of PDMS for VOCs relative to water is high. Even in cases where PDMS exhibits moderate selectivity, this material can still meet the requirements of most applications [26]. As can be seen from Table 1.1, PDMS has been used to remove a wide variety of VOCs from aqueous solutions.

A sampling of PV membrane materials which have been used for VOC removal from water are listed in Table 2.1. It should be noted that the same membrane material, but from different suppliers, could show different properties owing to variations in the degree of polymerization and production parameters.

2.6 Mass Transport Models of Pervaporation

A well established mass transport model is essential for engineering membranes separation processes. Unlike other membrane separation processes, mass transport through a pervaporation membrane process involves more complicated physiochemical interactions between permeants and the membrane. Several approaches have been proposed to describe the process.

2.6.1 Solution-Diffusion Model

The solution-diffusion model is accepted by the majority of membrane researchers [43].

According to this mechanism, pervaporation consists of three consecutive steps:

i.   Sorption of the permeant from the feed liquid to the membrane,

ii. Diffusion of the permeant on the membrane, and

iii. Desorption of the permeant to the vapor phase on the downstream side of the membrane.

Polymer	Structure	Reference
Polydimethylsiloxane (PDMS)	$(-Si(CH_3)_2-O-)_n$	[15,46]
Nitrile–butadiene copolymer (NBR)	$(-CH_2-CH=CH-CH_2-CH_2-CH(CN)-)_n$	[63]
Polyvinylidene fluoride (PVDF)	$(-CH_2-CF_2-)_n$	[62]
Styrene–butadiene (SBS)	$(-CH_2-CH=CH-CH_2-CH_2-CH-(C_6H_5)-)_n$	[63]
Polyolefin (PO)	$(-CH_2-CH_2-)_n$	[59]
Polyoctenamer	$(-(CH_2)_3-CH=CH-(CH_2)_3-)_n$	[62]
Poly[bis(phenoxy)phosphazene] (BPOP)	$-N=P((-O-C_6H_5)_2)-)_n$	[24]
Polyether-block-polyamides (PEBA)	$(-C(=O)-PA-C(=O)-C-PE-O-)_n$	[62]
Polyurethane (PUR)	$(-CONHR'NHCOORO-)_n$	[62]
Block copolymer styrene (PS) butadiene	$(-CH-(C_6H_5)-CH_2-)_m-(-CH_2-CH=CH-CH_2-)_n-(-CH-(C_6H_5)-CH_2-)_m$	[33]

Table 2.1: PV Membrane Materials used for VOC Removal

Ref: J.Hazard.Mater.B98 (2003) 76

It is illustrated in Fig 2.1. In general, solubility and diffusivity are concentration dependent. A number of mathematical equations for mass transport have been formulated on the basis of Fick's diffusion equation using different empirical expressions of concentration dependence of solubility and/or diffusivity. However, these equations cannot be taken for granted unless they are used within the experimentally established range for which the relationships expressed for diffusion and thermodynamic equilibria are applicable.
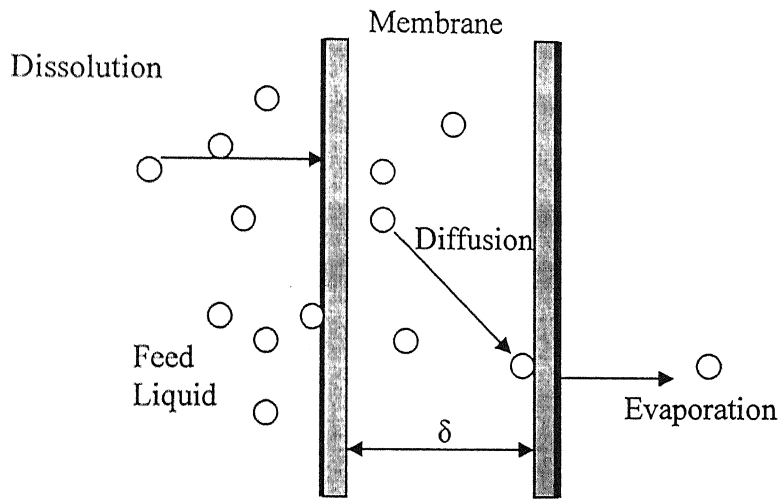
Fig 2.1: Schematic representation of Solution Diffusion Mechanism

Assuming that the diffusivities of individual permeants are proportional to the total concentration of permeants in the membrane, Green law et al [22] presented a simple model. However this model does not apply to nonideal cases such as alcohol water mixtures. On the same basis, a "six-coefficient exponential model" was proposed [23], but the significance of model parameters become suspect; and the model is of little predictive of interpretive. A more complex model was presented taking into consideration of the coupling effects on both sorption and diffusion [46, 48]. This model supposes the knowledge of diffusivity as a function of concentration, which is in fact one of the most difficult problems yet to solve in mechanistic approach. An alternative approach based on

an extension of the free-volume theory for diffusion in polymers was pursued later. Then it was modified by introducing the interaction parameters on the basis of Flory-Huggins thermodynamics and the effects of flux coupling [25].To facilitate mathematical treatment a different approach was presented [27], considering pervaporation as combination of liquid evaporation and vapor permeation. The normal solution diffusion model was simply applied to describe vapor permeation. But it was proved that this is not the case under any circumstances. Although, confirmations of solution-diffusion model have been accumulated for various boundary conditions; studies dealing specifically with the influence of downstream pressure on pervaporation fluxes are exceptions and remain somewhat controversial. The conspicuous unconcern of phase change in this explanation poses some questions.

2.6.2 Pore Flow Model

Recently a transport model was proposed on the basis of the pore flow mechanism [16]. It is assumed that there are a bundle of straight cylindrical pores on the membrane.
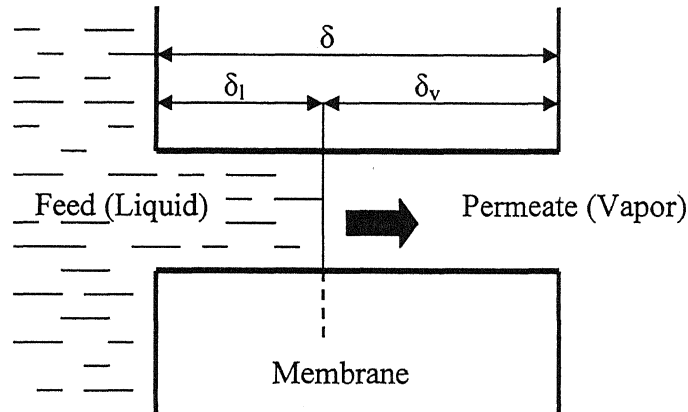
Fig 2.2: Schematic representation of Pore Flow Model

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The mass transport by pore flow mechanism also consists of three steps:

i. Liquid transport from the pore inlet to a liquid-vapor phase boundary,

ii. Evaporation at the phase boundary, and

iii. Vapor transport from the boundary to the pore outlet.

It is illustrated in Figure 2.2. In consideration that (i) the physical structure of the membrane is accounted for explicitly in the pore flow model, (ii) the position of the phase change of permeant in the membrane is clearly addressed in the pore flow model, (iii) several main features of pervaporation observed experimentally can be explained semi quantitatively by the pore flow model , and (iv) good models that enable description and prediction of pervaporation transport are still lacking, the pore flow model should be appreciated, although the present quantitative expression of the pore flow model is at a preliminary stage because some macroscopic concepts such as viscosity and friction constant are used in the derivation of the model equations, while fluid continuity does not necessarily hold when the pores are very small. Moreover the extensions of this model take into account of the vapour-liquid equilibrium data, without considering the change in vapor pressure itself with in a pore.

2.6.3 PPCSD Model

Using assumptions of thermodynamic equilibrium, simple concentration-dependent solubility, and diffusivity, a set of analytical equation were derived to express the pervaporation flux [19], which is called pseudophase-change solution diffusion model or PPCSD model. It assumes pervaporation is a combination of liquid permeation and vapor permeation mechanism in series. This is illustrated in figure 2.3. A pseudophase of permeant is located at the interface between these two mechanisms. The resultant equations were similar to that of pore flow model. This model was tested for its validity and showed good agreement with literature data in terms of the effect of feed pressure and permeate pressure. Comparison among three different membrane separation processes (namely, pervaporation, vapor permeation, liquid permeation) showed that the permeation flux is nearly same for pervaporation and vapor permeation processes under the assumption of thermodynamic equilibrium. On the other hand, the permeation flux for the liquid permeation process is always lower unless a certain high feed pressure is

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reached. But the assumption of pseudophase inside the membrane with same and simple relations of solubility and diffusivity holding for vapor and liquid permeation mechanisms is questionable. In liquid permeation zone, activity gradient is neglected, while for vapor, pressure contributions are neglected. Moreover the parameters used are assumed to be same in both zones.
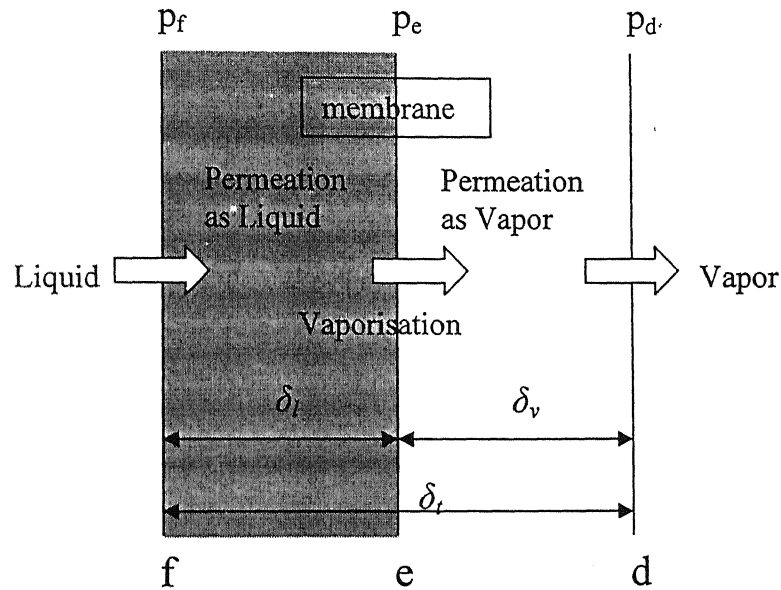
Fig 2.3: Schematic description of pseudophase change solution-diffusion (PPCSD) model

Although numerous models based on these above mentioned postulates have been proposed, many of them are solely based on qualitative observations and vigorous verification by experimental data is lacking. Each model works for some systems, but none is general enough to make good descriptions and predictions for most systems.

3.1 Pervaporation: process definition

Pervaporation, whose term derives from the two major integral operations involved in the separation process, namely, *permeation* and *evaporation*, is defined as a separation process in which a liquid feed mixture is separated by means of selective diffusion–vaporization through a non-porous membrane [23]. The feed liquid mixture which is to be separated is placed in contact with one side of the membrane. The feed liquid permeates through the membrane and the permeating liquid is removed as vapour from the downstream side. This is a passive process and the driving force for molecular or particle transport is the chemical potential difference. Permeate vapour is continuously removed to maintain the gradient using a vacuum pump or sweeping gas (normally air or steam) on the downstream side. The permeate vapour is condensed and collected or released as desired. Permeating components get vaporized by taking latent heat from feed liquid. Therefore, external heating is required to make up the loss of enthalpy and to maintain the isothermal conditions. A schematic diagram of the process is shown in figure 3.1.
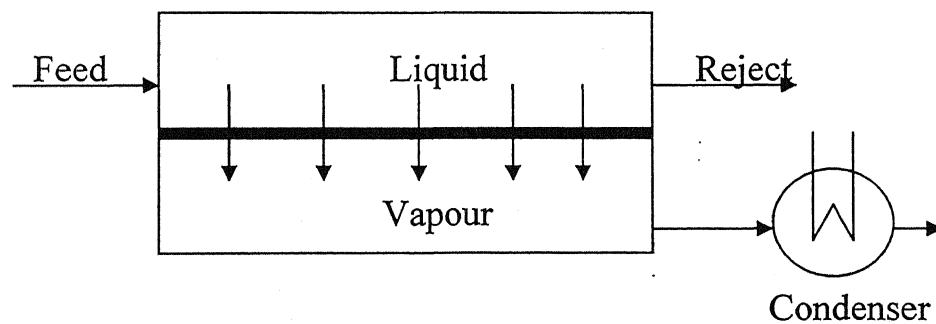
Fig 3.1: Schematic diagram of pervaporation process using vacuum

The PV membrane can be considered as a dense homogenous medium in which diffusion of species takes place in the free volume that is present between the macromolecular chains of the polymeric membrane material. VOCs encountered in an environmental remediation operation usually have concentrations in the range of 1–500 ppm (mg/L) [23]. Membranes used in pervaporation process are usually of the two types:

    i)   Hydrophobic membranes

    ii)   Hydrophilic Membranes.

Hydrophobic membranes show affinity to organics. So they are also called organophilic membranes. Certain membranes show affinity towards water and hence they are named hydrophilic membranes.

Each type of membrane will have its specific application. For separation of dissolved organics form aqueous streams hydrophobic membranes are used. As stated earlier VOCs present in a stream to be separated will be present in ppm levels. For its separation from aqueous stream the membrane should show affinity towards the organics. Hence hydrophobic membranes are used in its separation. The most commonly used hydrophobic membrane for VOC removal consists of a selective layer of polydimethylsiloxane (PDMS) [23].

Composite membranes are regarded as two layer system consisting of a nonporous membrane and a porous support; this latter structure being considered as a system of capillaries in parallel so that they offer zero resistance (Figure 3.2).

Separating layer ─┐   0.5 - 2 µm

Porous support   70 - 100 µm

Non-woven fabric   100 µm
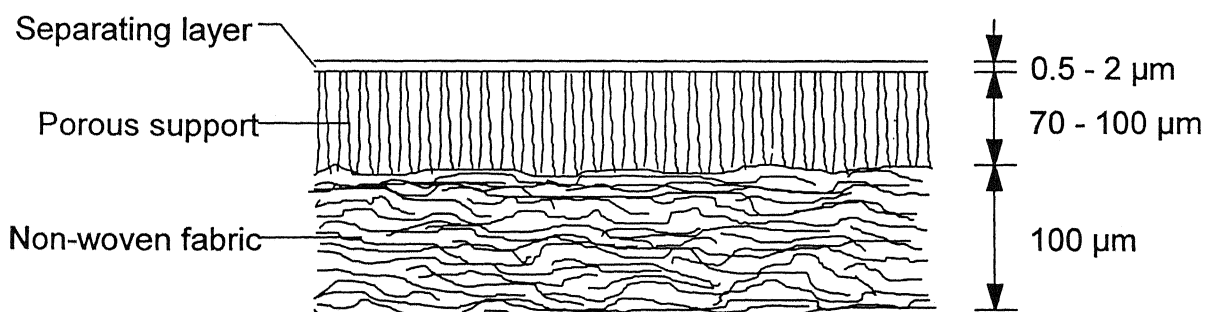
Fig 3.2: Cross-sectional presentation of a composite membrane

3.2 Chemical potential and activity

The most important partial molar quantity concerned in chemical thermodynamics is the partial molar free energy, a quantity known as the chemical potential. It is defined for a specified state of aggregation, a specified temperature, and an arbitrarily chosen but specified standard pressure [27]. One can use changes in chemical potentials to calculate changes not only in free energy, but also in work content, energy, enthalpy, and entropy, depending upon the constraints imposed on the processes, thus demonstrating its universality. Just like other membrane separation processes, in pervaporation also, the two sides of the membrane are subjected to two different environments, so that a chemical potential difference exists across the thickness of the membrane. Permeating liquid passes through the membrane from high chemical potential side to low chemical potential side.

The activity, a_i of a substance 'i', in a liquid or solid mixture is a quantity of single dimension defined in terms of chemical potential μ_i:

$$\mu_i = f_i(T) + RT \ln a_i \qquad (3.1)$$

where, $f_i(T)$ is a function of temperature, T only; and it is called the "standard chemical potential", μ_i^o. So, (3.1) is written as:

$$\mu_i = \mu_i^O + RT \ln a_i \qquad (3.2)$$

The ratio of activities of a substance in two different states, but at the same temperature will depend only on the difference in chemical potential. Before a numerical value can be assigned to activity, some kind of reference function must be assumed and some particular state must be chosen in which the activity approaches or equals the value of the reference function. If $g(\zeta)$ is a reference function, in which, ζ is a concentration, pressure, mole fraction, or some other similar variable that might be used in conjunction with temperature for describing the system, we can define generalized activity as,

$$\lim_{\zeta \to \zeta^*} \frac{a_i}{g(\zeta)} = 1 \qquad (3.3)$$

ζ^* is the value of ζ in the reference state, which is that state in which the activity equals the value of the reference function. As an example, consider a binary system for which x_i

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is the mole fraction of one of the components. Then, we say that the activity approaches the mole fraction as the solution becomes infinitely dilute,

$$\lim_{x_i \to 1} \frac{a_i}{x_i} = 1 \qquad (3.4)$$

Here the pure liquid is the reference state, and the activity of the pure liquid is equal to unity. Fugacity is a special kind of activity defined for conveniently dealing with the gases. It has all the attributes of activity; specifically, it involves the pressure as the reference function and zero pressure as the reference state. Fugacity concept can be extended to liquids and solids as well, by simply assigning to a liquid (or solid) a fugacity numerically equal to that of vapour in equilibrium with it. Obviously, a ratio between fugacity for any two states at the same temperature must be identical with the ratio of activities associated with the same two states regardless of what function the activity is referred to. Hence if we know the fugacity of a substance in each of two states, we can determine a ratio of activities for those two states. It one of those states is the reference state for activity, we can evidently determine the activity for the other state without difficulty. A similar argument can be applied to switching from one activity representation to another, without recourse to fugacity.

3.3 Material transport in the membrane

The diffusivity or diffusion coefficient D_{im} of a constituent in a solution is a measure of its diffusive mobility, and is defined as the ratio of its flux, J_i to its concentration gradient:

$$J_i = -D_{im} \frac{dc_i}{d\delta} \qquad (3.5)$$

which is Fick's first law written for the δ direction. The negative sign emphasizes that diffusion occurs in the direction of a drop in concentration. The diffusivity is a characteristic of a constituent and its environment like temperature, pressure, concentration, whether in a liquid, gas, or solid solution, and the nature of the other constituents [28]. The advantage of Fick's law is its extremely simple mathematical form. But it becomes a disadvantage, when dealing with highly non-ideal systems where .concentration dependency of diffusion coefficient is either unknown or highly

complicated. In this case the analogous form of Fick's law with the gradient of the chemical potential as driving force is the better choice:

$$J_i = - c_i m_i \frac{d\mu_i}{d\delta}$$

(3.6)

This is nothing, but a demonstration that flux should be equal to the product of concentration (c_i), thermodynamic diffusion coefficient or mobility (m_i), and driving force. Mobility is defined as the velocity per unit force on one mole of particles. Even for strongly non ideal systems, the mobility is much less (and in a much simpler form) concentration dependent than diffusivity [41]. In pervaporation, complicated concentration-dependent diffusion coefficients were always used to meet the experimental results in contrast to the almost negligible concentration dependency of the thermodynamic diffusion coefficient.

3.4 Separation Factor and Selectivity of a Membrane

The concentrations of the components i and j within the membrane at each interface will be proportional to the chemical potentials of components i and j in the adjacent fluids. We can express this chemical potential by the partial vapour pressures, p_i and p_j. On the feed side of the membrane, for a solution containing components i and j at the mole concentrations c_i and c_j , the chemical potential can be expressed as the partial pressure of the vapour in equilibrium with the feed solution. On the permeate side of the membrane, the chemical potential is the vapour pressure of i and j in the permeate gas stream [1].

For the each component of the solution we can write the normal Fick's law expression for the volume flux, J , through the membrane. Thus, for component i:

$$J_i = -D_i \frac{dc_i}{d\delta}$$

(3.7)

The transport mechanism of trace organics in an aqueous solution through a dense hydrophobic membrane by pervaporation may be described by five consecutive steps, as shown in Figure 3.3.

i). Diffusion of a penetrant from the bulk of the feed to the feed membrane interface

ii). Dissolution of the penetrant into the membrane

iii). Diffusion of penetrant through the membrane to the downstream side

iv). Desorption of the penetrant as vapour at the permeate side

v). Diffusion of penetrant from the vapour-membrane interface to the vapour bulk.
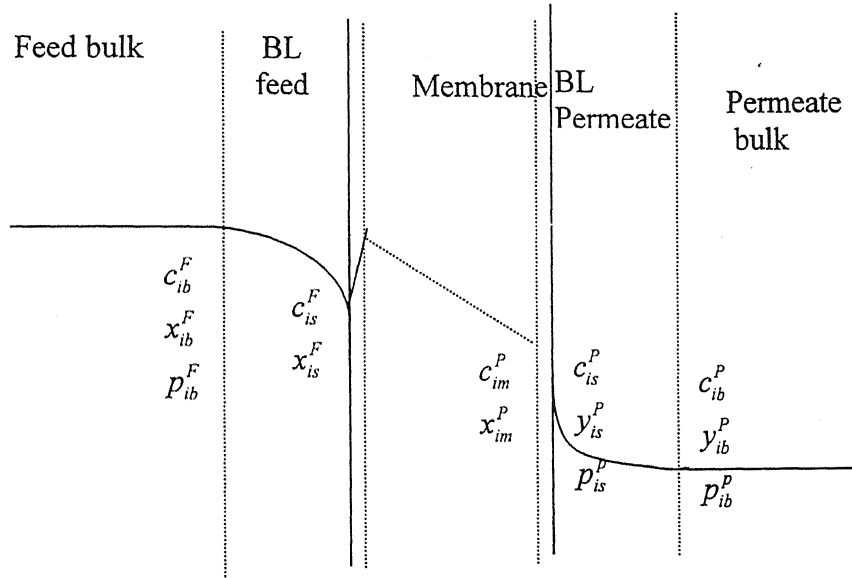
Fig 3.3: Mass transport steps during pervaporation process

The expression (3.7) can then be integrated over the membrane thickness l,

$$J_i = \frac{\overline{D}_i(c^F_{im} - c^P_{im})}{l} \tag{3.8}$$

Here, c^F_{im} and c^P_{im} are the concentrations of component i in feed and permeate interfaces of the membrane and $\overline{D}_i$ is the Diffusion coefficient of component i across the membrane which is assumed to be independent of concentration difference across the membrane. These concentrations are directly proportional to the partial pressure (p_i) of the component i in the adjacent fluids of the permeate [1]. Thus, we can write:

$$c^F_{im} = K_i \, p^F_{ib} \tag{3.9}$$

$$\text{and,} \quad c^P_{im} = K_i \, p^P_{ib} \tag{3.10}$$

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Where, K_i is the Henry's law partition coefficient p_{ib}^F and p_{ib}^P are the partial pressures of component i in the feed and permeate stream respectively. The, expression (3.8) then yields:

$$J_i = \frac{\overline{D}_i K_i (p_{ib}^F - p_{ib}^P)}{l}$$
(3.10)

Expressing the term $\overline{D}_i K_i$ as a permeability, P_i, we can write:

$$J_i = \frac{P_i (p_{ib}^F - p_{ib}^P)}{l}$$
(3.11)

Similarly for component j:

$$J_j = \frac{P_j (p_{jb}^F - p_{jb}^P)}{l}$$
(3.13)

Both to facilitate the mathematical treatment, and to understand the difference between pervaporation and evaporation, we consider the overall separation factor β_{pv}, achieved by a pervaporation process, as the product of an evaporation separation step β_{evap}, and a membrane separation step β_{mem} [1]:

$$\beta_{pv} = \beta_{evap} \, \beta_{mem}$$
(3.14)

That this is a justifiable approach can be seen by looking at the ratios of the components in each term. β_{pv} is given by the ratios of the proportions of components on the permeate and feed sides:

$$\beta_{pv} = \frac{p_{ib}^P / p_{jb}^P}{c_{ib}^F / c_{jb}^F}$$
(3.15)

here, β_{evap} represents the change in composition that would occur if the feed solution was to evaporate to form a hypothetical vapor phase, in equilibrium :with the feed solution, on the feed side of the membrane, i.e.:

$$\beta_{evap} = \frac{p_{ib}^F / p_{jb}^F}{c_{ib}^F / c_{jb}^F}$$
(3.16)

where, β_{mem} expresses the ratio of the components of the hypothetical feed vapor and the permeate vapor, thus:

$$\beta_{mem} = \frac{p^P_{ib}/p^P_{jb}}{p^F_{ib}/p^F_{jb}} \tag{3.17}$$

Combining the express ions for β_{evap} and β_{mem} leads back to our definition of β_{pv}.

Expression (3.14) does not imply that the pervaporation process actually occurs as an evaporation step followed by a permeation step. However, (3.14) does make clear that the partial vapor pressures of the feed liquid have a direct impact on the separation achieved by the pervaporation process. The reason is that the partial vapor pressures of the feed liquid represent the driving force for the membrane permeation step [1].

A mass balance of component i, in the feed side boundary layer over membrane surface may be obtained at steady state. The sum of convective and diffusive flux towards membrane surface is equal to the permeate flux of component i [29].

$$v_p x^F_i - D^F_i \frac{dx^F_i}{dz} = v_p y^P_{ib} \tag{3.18}$$

where, v_p $(=N/\rho)$ is the velocity of the fluid perpendicular to the membrane surface, This equation is obtained after assuming that the permeate side boundary layer is neglected due to low down stream pressure.

In the expression (3.15) the partial pressures of the components i and j are not directly measurable. We have to get a measurable quantity for calculating the separation factor. Expression (3.17) is integrated with the following boundary conditions.

$$z=\delta; \ x^F_i = x^F_{is} \ \& \ z=0; \ x^F_i = x^F_{ib}$$

The actual separation factor of pervaporation process is calculated based on measurable concentrations of feed and permeate, according to

$$\beta^{act}_{ij} = \frac{y^P_{ib}/y^P_{jb}}{x^F_{ib}/x^F_{jb}} \tag{3.19}$$

where, y_{ib}^{P} and y_{jb}^{P} are the mass fraction of components i and j in the permeating vapour which is collected by condensation.

For the separation of VOCs from aqueous stream it is important to find the relative separation between the organics and water which is present in bulk amount compared to the organics concentration whose concentration is of the order parts per million (ppm). This is called the Selectivity of the membrane. Thus Selectivity is the measure of hydrophobicity of the membrane. Mathematically, the selectivity of component i can be calculated as given in expression (3.19).

$$\alpha_{iw}^{act} = \frac{y_{ib}^{P}/y_{wb}^{P}}{x_{ib}^{F}/x_{wb}^{F}} \approx \frac{y_{ib}^{P}}{x_{ib}^{F}}; \quad (\because y_{wb}^{P} = x_{wb}^{F} \cong 1.0) \tag{3.20}$$

Here the second component j in expression (3.19) is water and is represented as w, as water is present in bulk quantity $y_{wb}^{P} = x_{wb}^{F} \cong 1.0$.

3.5 Influence of concentration on flux and separation factor

The mass transfer across the boundary layer on the feed side can be described by,

$$N_i = k_{L,i}(c_{ib}^{F} - c_{is}^{F}) = k_{x,i}(x_{ib}^{F} - x_{is}^{F}) \tag{3.21}$$

The mass transfer across the membrane is described by Ficks law,

$$J_i = -C_i D_i \frac{d\ln a_i}{dz} \tag{3.22}$$

Further, the activity inside the membrane can be described as the product of the activity coefficient γ_i and the mole fraction x_i. At low concentrations, activity coefficient inside the membrane may be considered to be constant and therefore,

$$J_i = -\frac{C_i D_i}{x_i} \frac{dx_i}{dz} \tag{3.23}$$

In terms of molar density, ρ Eq (3.22) may be rewritten as,

$$N_i = -\rho D_i \frac{dx_i}{dz} \tag{3.23}$$

Integration of eq (3.23) across the membrane (considering the concentrations in the membrane) leads to eq (4.15) as,

$$N_i = -\rho \frac{\overline{D_i}}{l}(x_{im}^P - x_{im}^F) \tag{3.24}$$

where, $\overline{D_i}$ is the mean diffusion coefficient through the membrane. Solution-diffusion model assumes that equilibrium is at both sides of membrane interfaces include the sorption and the desorption steps. At equilibrium, chemical potential at the membrane interface is equal to the chemical potential inside the membrane. This condition is same for both feed and permeates sides. Thus, activities also get related in the same way for constant pressure in the membrane.

$$\mu_{is}^F = \mu_{im}^F \Rightarrow a_{is}^F = a_{im}^F \tag{3.25}$$

$$\mu_{is}^P = \mu_{im}^P \Rightarrow a_{is}^P = a_{im}^P \tag{3.26}$$

Further, assuming that the vapours in the permeate side behave as ideal gas,

$$a_{is}^F = \gamma_{is}^F x_{is}^F \tag{3.27}$$

and $\quad a_{is}^P = \dfrac{p y_{is}^P}{p_i^o} = \dfrac{p y_{ib}^P}{p_i^o} \tag{3.28}$

Equation (3.28) was obtained assuming the ratio of fugacity coefficients as well as *Poynting factor* to be equal to one. Hence, the concentrations inside the membrane for both sides can be obtained by combining eqs (3.25), (3.26), (3.27) & (3.28) and therefore,

$$x_{im}^F = \frac{\gamma_{is}^F}{\gamma_{im}^F} \cdot x_{is}^F \tag{3.29}$$

$$x_{im}^P = \frac{p}{p_i^o} \frac{y_{ib}^P}{\gamma_{im}^P} \tag{3.30}$$

The molar flux is then obtained by inserting eqs (3.29) and (3.30) into eq (3.24); accordingly,

$$N_i = \frac{\rho \overline{D_i}}{l \; \gamma_{im}^F p_i^o}(\gamma_{is}^F x_{is}^F \, p_i^o - p \, y_{ib}^P) = k_{m,i}(x_{is}^F H_i - p_{ib}) \tag{3.31}$$

Eq (3.31) was obtained assuming the activity coefficient throughout membrane is a constant. Further, Henry's law constant $H_i = p_i^O \gamma_{is}^F = p_i^O \gamma_{ib}^F$ and mass transfer coefficient

$$k_{m,i} = \frac{\overline{P}_{m,i}}{l} \qquad (3.32)$$

Analogous to gas separation, it is convenient to define an overall pervaporation flux in terms of vapour pressure difference as,

$$N_i = \frac{\overline{P}_i}{l}(p_i^O \gamma_{ib}^F x_{ib}^F - p_{ib}) = K_{x,i}(x_{ib}^F - \frac{p_{ib}}{H_i}); \text{ where } K_{x,i} = \frac{\overline{P}_i H_i}{l} \qquad (3.33)$$

At steady state, flux through each layer is same, and therefore, the overall mass transfer coefficient may be related to film mass transfer coefficients,

$$\frac{1}{K_{x,i}} = \frac{1}{k_{x,i}} + \frac{1}{H_i k_{m,i}} \qquad (3.34)$$

Further, the molar concentration based overall mass transfer coefficient and mole fraction based mass transfer coefficient are related by $K_{L,i} = K_{x,i}/\rho$. In the case of downstream pressure tending to zero ($p \to 0$), eq (3.33) becomes,

$$N_i = K_{x,i} x_{ib}^F \qquad (3.35)$$

Expressions (3.33) and (3.35) shows that the molar flux of component i is proportional to its concentration in the feed.

3.6 Modeling and Simulation

In the case of ternary system the ordinary diffusion equation (Fick's Law) does not work. The mechanical statistics equations like the Stefan – Maxwell relationship are particularly suitable for the computation of multi-component diffusion with coupling between the fluxes. When concentration gradients are applied one has to know the multi-component equilibrium law between the binary mixture and the polymer. The knowledge of the activity versus volume fraction relationship is well described by statistical mechanics approaches (Flory-Huggins theory) for one ideal solvent swelling an amorphous polymer. But for multi-component mixtures, no such equilibrium relationship has been verified even for ideal cases.

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Thus, the equation for flux can be obtained from the generalised multi-component Stefan – Maxwell equation

$$-\frac{\nabla \mu_i}{RT} = \sum_{j=1}^{j=n} \frac{c_j}{cD_{ij}} \left[\frac{J_i}{c_i} - \frac{J_j}{c_j} \right], \quad c = \sum_{j=1}^{j=n} c_j \tag{3.36}$$

where J_i is the average diffusive molar flux of species i, n the number of species in the mixture, c_i the morality of species i, R the ideal gas constant, T the absolute temperature and $\nabla \mu_i$ the gradient of the chemical potential. The D_{ij} are generalizations of Stefan–Maxwell diffusivities and have the symmetrical property ($D_{ij} = D_{ji}$). Rearranging this equation leads to the generalized Fick's equation:

$$J_i = -c_i D_i \frac{\nabla \mu_i}{RT} + x_i \sum_{j=1}^{j=n, j \neq i} \alpha_{ij} J_j \tag{3.37}$$

with

$$D_i = \frac{c}{\displaystyle\sum_{j=1}^{j=n, j \neq i} c_j \Big/ D_{ij}} \tag{3.38}$$

and

$$\alpha_{ij} = \frac{D_i}{D_{ij}} \tag{3.39}$$

Now, from phenomenological approach of thermodynamics

$$\nabla \mu_i = \nabla \mu_i^0 + RT \ln C_i \tag{3.40}$$

So, above equations gives

$$J_A = -D_A \frac{dC_A}{dz} + J_B \frac{D_A}{D_{AB}} \frac{C_A}{\left(C_A + C_B\right)} \tag{3.41}$$

$$J_B = -D_B \frac{dC_B}{dz} + J_A \frac{D_B}{D_{AB}} \frac{C_B}{\left(C_A + C_B\right)} \tag{3.42}$$

Component A has a higher permeability than component B. In water treatment, A represents the organic component and B is water.

In general

$$J_i = -D_i \frac{dC_i}{dz} + J_j \frac{D_i}{D_{ij}} \frac{C_i}{\left(C_i + C_j\right)} \tag{3.43}$$

We suppose that the diffusivity of each component depends only on the concentration of the key component.

$$D_{i,m} = D^0_{i,m} \exp(\varphi_{iA} C_{A,m} + \varphi_{iB} C_{B,m}) \tag{3.44}$$

So, this gives

$$-D^0_{i,m} \exp(\varphi_{iA} C_{A,m} + \varphi_{iB} C_{B,m}) \frac{dC_{im}}{dz} = J_i \left[1 - \frac{J_j}{J_i} \frac{D^0_i \exp(\varphi_{ii} C_{i,m} + \varphi_{ij} C_{j,m})}{D_{ij}} \frac{C_{im}}{C_{im} + C_{jm}} \right] \tag{3.45}$$

Let

$$\beta_{ij} = \frac{J_j}{J_i} \frac{D^0_i \exp(\varphi_{ii} C_{i,m} + \varphi_{ij} C_{j,m})}{D_{ij}} \frac{C_{im}}{C_{im} + C_{jm}} \Rightarrow \textit{Effective coupling factor} \tag{3.46}$$

So,

$$-D^0_{i,m} \exp(\varphi_{iA} C_{A,m} + \varphi_{iB} C_{B,m}) \frac{dC_{im}}{dz} = J_i [1 - \beta_{ij}] \tag{3.47}$$

or,

$$-D^0_{i,m} \exp(\varphi_{iA} C_{A,m} + \varphi_{iB} C_{B,m}) \frac{dC_{im}}{dz} \frac{\left(C_{i,1m} - C_{i,2m}\right)}{\left(C_{i,1m} - C_{i,2m}\right)} = J_i \left[1 - \beta_{ij} \right] \tag{3.48}$$

Substituting above equations and integrating, gives the flux of component i:

$$D^0_{i,m} \frac{\left(C_{i,1m} - C_{i,2m}\right)}{\delta_m} R_i = J_i \left[1 - \beta_{ij} \right] \tag{3.49}$$

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where,

$$R_i = \frac{1}{\left(C_{i,1m} - C_{i,2m}\right)} \int_{C_{i,2m}}^{C_{i,1m}} \exp(\varphi_{ii} C_{i,m} + \varphi_{ij} C_{j,m}) dC_{i,m} \qquad (3.50)$$

The adsorption concentrations on both surfaces of the membrane top layer, $C_{i,1M}$ and $C_{i,2M}$, are determined from the assumption of thermodynamic equilibrium. The adsorption concentration on the feed side of the membrane is proportional to the component activity in the phase adjacent to the membrane:

$$C_{i,1m} = \psi_{i1} \frac{p_{i1}}{p_i^0(T_1)} \qquad (3.51)$$

On the downstream side, thermodynamic equilibrium yields the following equation:

$$C_{i,2M} = \psi_{i2} \frac{p_{i2}}{p_i^0(T_2)} \exp\left[-\frac{V_i}{RT_2}\left(p_1 - p_i^0(T_2)\right) \right] \qquad (3.52)$$

in which ψ_{i1} and ψ_{i2} are partition coefficients for component i at the feed side surface and the permeate side surface of the top layer, respectively. The term p_i^0 (T_2) is the saturation vapor pressure of pure component i at the permeate side temperature.

The vapour flux through the membrane support layer is expressed as:

$$J_i = \frac{D_{i,V}}{XRT_2}\left(p_{i,2} - p_{i,3}\right) \qquad (3.53)$$

where $p_{i,2}$ and $p_{i,3}$ are the partial pressures of component i at the evaporation surface and in the bulk vapour, respectively. The latter depends on permeate concentration of component i:

$$p_{i,3} = P_3 \frac{J_i}{J_A + J_B} \qquad (3.54)$$

The diffusion coefficient of component i in the porous support, $D_{i,v}$ is estimated by a combination of molecular diffusion and Knudsen diffusion components:

$$\frac{1}{D_{i,V}} = \frac{\tau}{D_{AB}\varepsilon} + \frac{1}{D_{i,K}} \qquad (3.55)$$

Here ε is the porosity of the support layer (void volume/total volume) and τ is the tortuosity of the support layer. DAB is the molecular diffusion coefficient determined from the Fullor, Schetteler and Giddings equation:

$$D_{AB} = \frac{1.013 \times 10^{-4} T_2^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}}{P_3 \left[(\Sigma J)_A^{1/3} + (\Sigma J)_B^{1/3} \right]^2} \sqrt{b^2 - 4ac} \tag{3.56}$$

While the Knudsen diffusion coefficient, $D_{i,K}$, is calculated from the kinetic theory of gases as :

$$D_{i,K} = 97r \sqrt{\frac{T_2}{M_i}} \tag{3.57}$$

For the solvent, the feed side resistance is negligible. Combining above equations gives:

$$J_i \left[1 - \beta_{ij} \right] = \frac{D_{i,m}^0 R_i (\psi_{i1} p_{i1} - \psi_{i2} p_{i2})}{\delta_m p_i^0} \tag{3.58}$$

In the pervaporation of dilute solutions, such as water containing trace organic compounds, the solute concentration is usually low, and the membrane has a high selectivity for the solute, The permeate flux is therefore low. The following assumptions appear to be reasonable:

1. Low temperature difference across the membrane:

$$T_2 \approx T_1$$

2. Henry's law is valid for the solute (low concentration):

$$p_{A1} = H_A C_{A,1}$$

3. Vapor pressure of the solvent in the feed solution approximates that of the pure solvent.

4. Partition coefficients of the components are constant across the top layer.

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Defining the top layer permeability of component i as:

$$L_i = \psi_i D^0_{i,m} R_i \tag{3.59}$$

and eliminating p_{i1} and p_{i2}, the following equations can be derived:

$$J_A = \frac{\left(C_{AL} - \dfrac{P_3}{H_A}\dfrac{J_A}{J_A + J_B}\right)}{\dfrac{1}{k_L} + \dfrac{\delta_m p^0_A}{L_A H_A}\left(1 - \beta_{AB}\right) + \dfrac{1}{H_A k_{AV}}} \tag{3.60}$$

$$J_B = \frac{\left(1 - \dfrac{P_3}{p^0_B}\dfrac{J_B}{J_A + J_B}\right)}{\dfrac{\delta_m}{L_B} + \dfrac{1}{p^0_B k_{BV}}} \tag{3.61}$$

where $k_{A,V}$ and $k_{B,V}$ are the mass transfer coefficients of vapor components within the membrane support layer, defined by:

$$k_{A,V} = \frac{D_{A,V}}{X R T_2} \tag{3.62}$$

$$k_{B,V} = \frac{D_{B,V}}{X R T_2} \tag{3.63}$$

As feed side concentration polarization may be expressed simply from the difference between the concentrations in the bulk feed and at the liquid-membrane interface:

$$J_A = k_L \left(C_{A,L} - C_{A,1}\right) \tag{3.64}$$

Two assumptions are implied in this equation. First, the diffusion coefficient of the solute in the boundary layer is independent of solute concentration, and second the solute convective flux is negligible (accurate for dilute solutions).

The liquid film mass transfer coefficient, k_L, is conventionally described using an empirical correlation of the form:

$$Sh = aRe^m Sc^n$$

(3.65)

Here Sh is the Sherwood Number; Re is the Reynolds Number and Sc Schmidt Number. *a, m,* and *n* are constants defining the flow in the system. At the membrane-liquid interface, thermodynamic equilibrium is assumed to establish rapidly, thus presenting no resistance to transport.

4.1 Materials and Chemicals

a) Membrane: PERVAP® - Teflon coated PDMS polymeric composite membrane; supplied by PERVATECH, Netherlands.

a) Benzene (99.9 wt%), Ranbaxy (India) Limited, Worli, Bombay

a) Toluene (99.9 vol%), Qualigens Fine Chemicals, Mumbai

a) Phenol (99.5 wt%), Ranbaxy (India) Limited, Worli, Bombay

a) N-Hexane (99.5 wt%), Ranbaxy (India) Limited, Worli, Bombay

a) Silicon Elastomer, SYLGARD 184, U.S.A

a) Poly-Dimethyl Siloxane polymer liquid (PDMS), Aldrich Chemical Co., U.S.A.

a) Liquid Nitrogen, supplied from Liquid N_2 plant, IIT-Kanpur

4.2 Instruments and other auxiliary accessories:

a) Cell

The pervaporation test cell is made of glass consisting of a pair of "cups" kept face to face so that the membrane can be secured in between with the help of specially designed flanges (Figure 4.1). One such "cup" has an approximate diameter of 90 mm, and a length of 100 mm to provide an approximate volume of 400 ml. It provides an effective membrane area of 50.4 cm^2.

b) Peristaltic Pump

- Model – Miclins, VSP 100, Rollers – 4, Tube size supported – 4mm to 8mm bore size wall thickness 1.5 mm

- Flow rate – 0.15 L/min -1.5 L/min (+/- 3% accuracy) and Max. Speed – 1500 rpm (Forward/Reverse)

c) Vacuum Pump

- Type – Double stage Rotary vacuum pump VT 2012, Motor – 0.5 H.P., Vacuum Techniques Pvt. Ltd., Bangalore, Oil Charge – 0.75,

- Pumping speed -- 250 L/min, R.P.M. – 1440

d) Pirani Guage

- Model – VT-DHP-11, Vacuum Techniques Pvt. Ltd., Bangalore.

e) PID - Controller

- Model – 1) TIC-03, Blue Bell 2) PG16, Fuji, Japan
- Range – 0-200 ^{0}C and accuracy - ± 0.1 ^{0}C

f) Weighing Balance

- Afcoset electronic balance, Accuracy – 0.0001 g

g) Gas Chromatograph

- Nucon-5700
- Data station and software - (AIMIL, Delhi)
- FID, Flame Ionization Detector with Column - ChWhP 101

h) Homogenizer

- Model: D-8, ART- MICCRA, Switzerland

4.3 Analysis of Benzene -Toluene -Water mixtures

Benzene -Toluene -Water mixtures were analyzed using gas chromatograph. For the analysis of the system Flame Ionization Detector (F.I.D) was used. The carrier gas used was nitrogen. A mixture of hydrogen and air was used as the fuel. The G.C. conditions were set by trial and error for getting distinguished peaks of water and alcohols. The settings used are given below:

System	Oven temperature, ^{0}C	Detector Temperature, ^{0}C	Injector Temperature, ^{0}C	Main Column Pressure, kg/ cm^2
Benzene -Toluene -Water	200	220	210	3.5

Table: 4.1 - Conditions set for gas chromatography during the analysis of Benzene - Toluene -Water mixtures

The calibration curve was prepared by calculating the ratio of areas under the peaks of components present and plotting them against their concentrations. Calibration data and curves have been shown in appendix A

controllers to control the temperatures on both sides within ± 0.1°C error. The feed liquid was taken in a container and was kept at 30°C. A schematic diagram of the set-up is shown in Figure 4.1

A peristaltic pump was used to circulate the feed liquid through the cell. Once the recirculation started, vacuum was simultaneously applied on the downstream side. At the same time liquid trap was inserted in the Dewar-flask filled with liquid nitrogen. Liquid permeated through the membrane was then recovered in the liquid trap. The condenser system consisted of two traps that could be used alternately; allowing for the collection of permeated stream continuously without interruption of the operation during the weight measurements. When sufficient quantity of pervaporate was accumulated in the trap, the paths were interchanged. For this, the valves of the operating channel were closed first. The Dewar-flask was then taken out from the first channel and placed in the second channel and all valves in this second root were opened. The experiment was continued until a pseudo steady state condition was reached, i.e., when consecutive fluxes became equal.

The permeated compound would be obtained in frozen form (since the temperature of liquid nitrogen is -185.5°C). So when the Dewar-flask is taken out, the liquid trap gets exposed to atmosphere and sample melts. So obtained samples were measured in a four decimal accurate weighing balance to determine the flux. Then these samples were analyzed in a Gas Chromatograph to estimate the concentration of each component.

4.4.2 Pervaporation Experiments at different VOC Concentration

Pervaporation experiments were conducted at different VOC feed compositions. The experiments were conducted for the following proportions of organics in aqueous medium.

i)   400 ppm of total organic concentration

ii)   600 ppm of total organic concentration

iii) 800 ppm of total organic concentration

iii) 50-50 Benzene – Toluene Aqueous solution
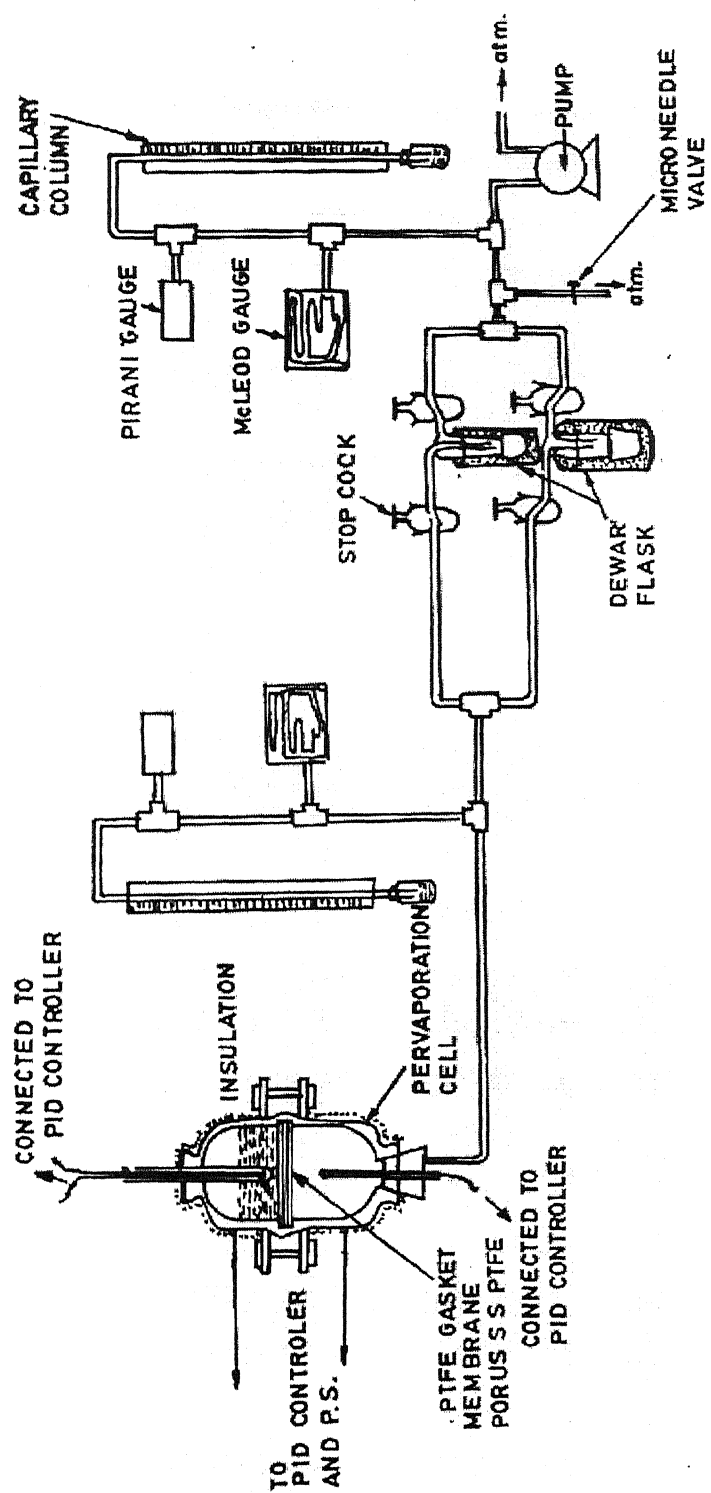
Fig 4.1: Schematic diagram of pervaporation experimental setup

CAPILLARY COLUMN

PIRANI GAUGE

McLEOD GAUGE

STOP COCK

DEWAR FLASK

atm.

PUMP

MICRO NEEDLE VALVE

atm.

CONNECTED TO PID CONTROLLER

INSULATION

PERVAPORATION CELL

TO PID CONTROLLER AND P.S.

PTFE GASKET

MEMBRANE

PORUS S S PTFE

CONNECTED TO PID CONTROLLER

All the experiments were conducted at room temperature, i.e. around 30°C. The experiments were meant to find out the influence of change in concentration of benzene and toluene on flux and separation factor and to find out the effect of coupling in the case of multi-component systems on pervaporation. Therefore, apart from composition of feed mixture, all other parameters were kept constant for experimentations. A vacuum of 2 mm of Hg was applied at the permeate side for all experiments. The flow rates of the feed solution for the experiments were maintained at 6.25 mL/s. It could be achieved by maintaining the speed of the peristaltic pump at 400 rpm.

Volatile organic compounds (VOCs) constitute major fractions, as contaminants (particularly chlorinated and aromatic hydrocarbons) in industrial waste waters, especially from petrochemicals industries. Conventional separation technologies such as distillation and liquid- liquid extraction are having problems due to the large volumes of the waste streams. It is in this regard that the process of pervaporation finds a place in researchers mind to examine potentials of such separations and recoveries of valuable organics. The solubility and diffusivity of the feed liquid in the membrane are the dominant factors determining the rates and separation characteristics of the pervaporation system. Most of the VOCs in aqueous solution at a particular composition are able to permeate selectively through pervaporation dense membranes without much hindrance or without depicting any significant change (in terms of usual flux and selectivity trend with operating conditions) during their permeation. Whether or not such a change (in other observable or measurable parameters) is there for components permeating individually with change in parameters may be an interesting phenomenon to be examined. Therefore, in order to do such an examination, it was decided to carry out experiments/studies by changing the composition of the feed solution. From the literature review, it was clear that many studies have been conducted for binary mixtures of different VOCs with water. However, in general, there will be more than one VOC in the wastewater stream. Thus, the objective was to study the separation of multi-component VOCs in aqueous solution. Two major VOCs, which are present in wastewater stream of most of the industries, are benzene and toluene. Even though they occupy the first two places in the homologous series and hence have similar properties, the separation of these VOCs from water becomes an energy intensive task with conventional methods of separation; particularly, if the concentrations are in ppm levels. Therefore, objective was to study the effect of change in concentrations of benzene and toluene in the feed solution on flux and selectivity. With the use of hydrophobic membrane, there was an increase in organic flux with the increase in organic concentration in the feed. Further, another objective of the study was to find the coupling effect, as there are two competing organics to be

separated. It was found that the hydrophobic teflon coated composite poly-dimethyl siloxane (PDMS) membrane was more selective to benzene than toluene. The coupling effect tends to produce a maximum in selectivity for the organics at a particular composition.

Pervaporation experiments were conducted at different VOC feed compositions. Following proportions of organics in aqueous medium were chosen for experiments:

i)   400 ppm of total organic concentration

ii)   600 ppm of total organic concentration

iii)   800 ppm of total organic concentration

iv)   Equal concentration of benzene and toluene in aqueous solution

Following paragraphs, therefore, present and discuss the salient results of separation of multi-components VOCs, benzene and toluene, from aqueous stream with change in concentration of the organics in feed solution.

5.1 Total organic concentration: 400 ppm

A feed mixture containing 400 ppm of total organics (ie Benzene and Toluene) in aqueous medium was separated using PERVATECH Teflon coated composite Poly-Dimethyl Siloxane (PDMS) membrane at an ambient temperature of 30°C. Experiment was continued until pseudo steady state flux was obtained. The system reached pseudo steady state after 2 hours.

Experiments were carried out at different benzene and toluene composition and have been given in Table 5.1 (maintaining the total organic content in the medium 400 ppm). It may be noted that the total organic load on the membrane remains the same. Fig. 5.1 shows the total organic selectivity variation with change in benzene concentration in the organics. Selectivity of the membrane is defined by the Eqn. 3.20. It is observed that a maximum is reached in the selectivity of the membrane when it is plotted as a function of percent of benzene in the organics in the feed. There is an increase in the selectivity of the membrane in the presence of two components in the system as compared to single component. It is clear from the Fig. 5.2 that the selectivity of binary mixture of benzene in aqueous medium is greater than that with binary mixture of toluene in aqueous medium. Thus the PDMS membrane is more selective to benzene than toluene. Driving

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force for mass transfer in pervaporation is the partial pressure difference of the components across the thickness of the membrane. Separation of components depends on the volatility of the components and also the preferential selectivity of the membrane.

Table 5.1: Concentration of benzene and toluene for 400ppm total organics

Experimental Run	Benzene Concentration (ppm)	Toluene Concentration (ppm)
1	400	0
2	300	100
3	200	200
4	100	300
5	0	400

The membrane is selective to both the components as compared to water. The mass transfer driving force gets shared between them, according to their relative volatilities. Further, for two competing components the driving force of one of the components may affect the transfer of the other component. This phenomenon is called coupling. In the present case, the mass transfer driving force of water is shared by organic components. Thus due to coupling effect the organic components get extra driving forces. This is the reason there is an increase in selectivity for both the organic components, as evidenced from Fig 5.1. The change in total flux (ternary mixture) across the membrane with benzene composition is shown in Fig.5.2. There is a decrease in steady state flux with change in benzene concentration and a minimum is reached. As the membrane becomes more selective to organics, there will be a decrease in water flux across the membrane (as it is less selective). Therefore, a decrease in total flux is observed because of decrease in water flux which is present in large quantity in the feed compared to organics (present only in ppm levels). Fig. 5.3 depicts the change in separation factor for benzene with the change in concentration of benzene in the feed.

Total Organic Selectivity Vs Benzene % in Organics

Fig 5.1: Variation in total selectivity with benzene concentration for 400 ppm organic concentration

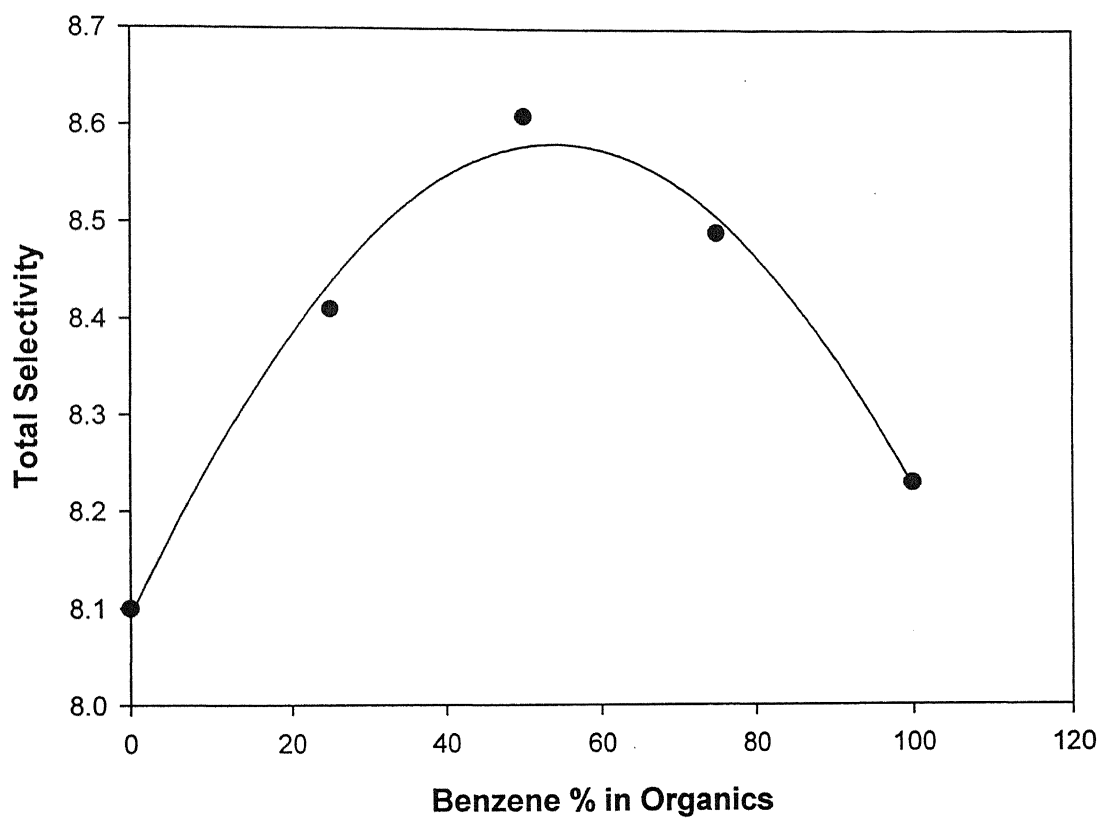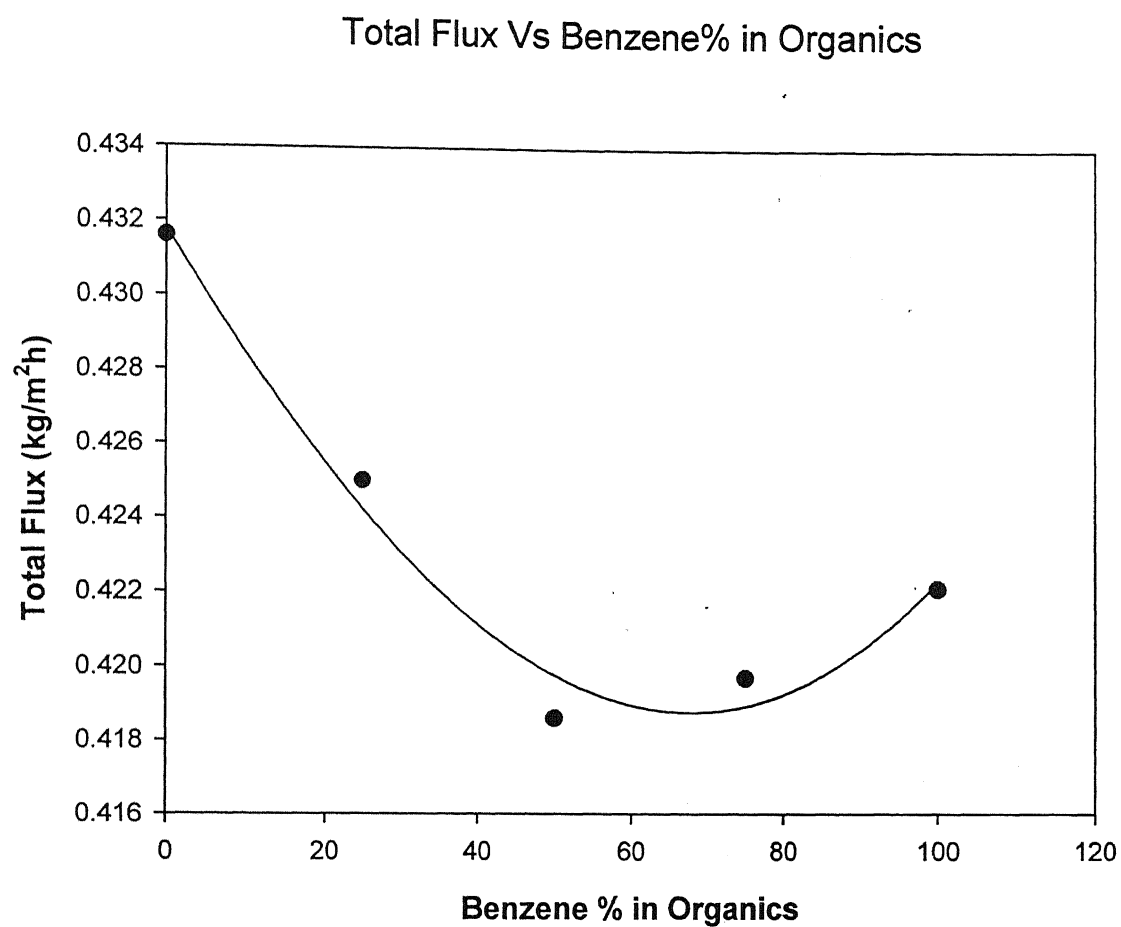**Fig 5.2: Variation in total flux with benzene concentration for 400 ppm organic concentration**
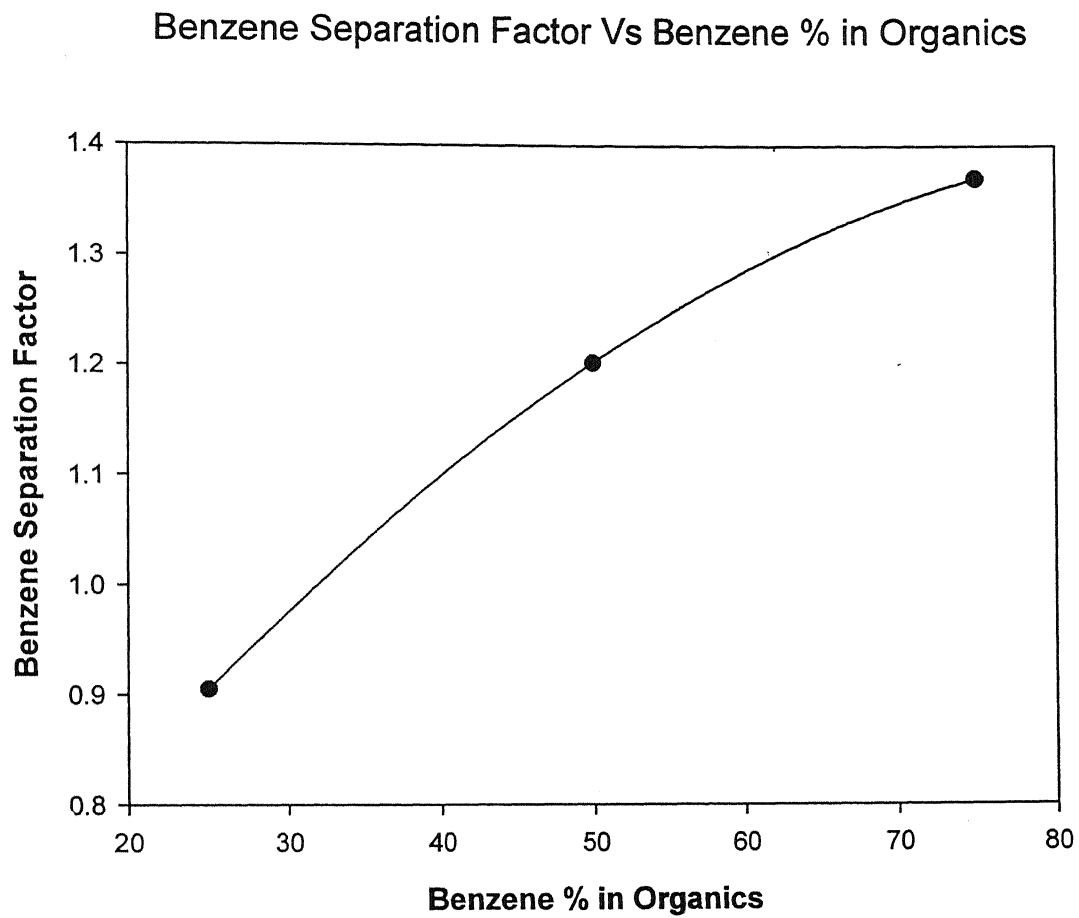
Fig 5.3: Variation in benzene separation factor with benzene concentration for 400
ppm organic concentration

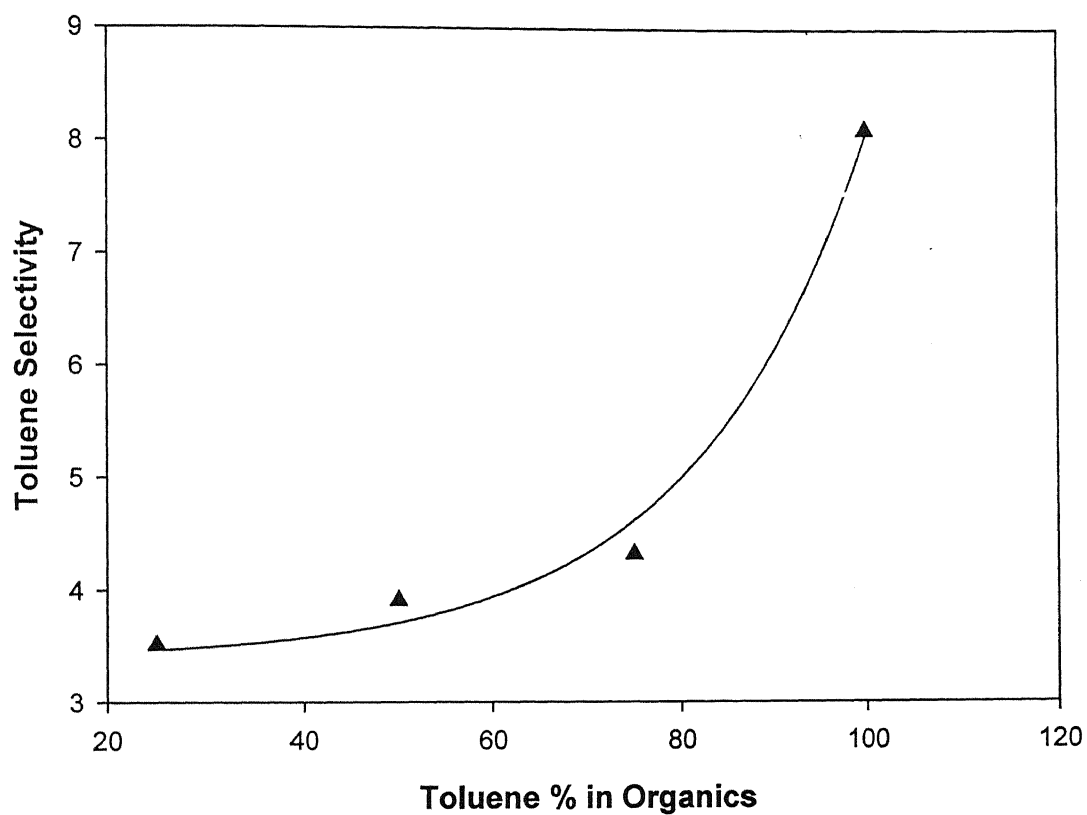Toluene Selectivity Vs Toluene % in Organics

Fig 5.4: **Variation in toluene selectivity with benzene concentration for 600 ppm organic concentration**

It is already clear that the membrane is more selective towards benzene. However, if the concentration of benzene is less (i.e. 25% of total organics present in the feed) its separation factor becomes less than one. Accordingly, at low concentration of benzene toluene passes preferentially through the membrane. But as the concentration of benzene increases to a comparable amount to that of toluene (i.e. similar concentrations of benzene and toluene – around 200 ppm each) the separation factor of benzene then attains a value of 1.2. Thus with the increase in benzene concentration in the feed (as the membrane is selective towards benzene) there is an increase in separation factor of benzene.

In Fig.5.4, toluene selectivity is plotted as a function of toluene concentration. It is observed that there is gradual increase in selectivity with increase in concentration of toluene (in the organics in the feed). However, if the feed contains only toluene then the selectivity is much higher. As mentioned earlier, in multi-component VOC solution, the mass transfer driving force is shared between the components. So there is a competitive separation between the components, apart from the selectivity with respect to water. But in single component system there is no sharing of driving force. So its selectivity will be higher as observed experimentally from results shown in Fig 5.4.

5.2 Total organic concentration: 600 ppm

A feed mixture containing 600 ppm of total organics (i.e. benzene and toluene in aqueous medium) was separated using PERVATECH Teflon coated composite Poly-Dimethyl Siloxane (PDMS) membrane at a temperature of 30°C. Experiment was continued until pseudo steady state flux was obtained. The system reached pseudo steady state after 2 hours. Permeate concentrations were analyzed and the results are discussed below.

An experimental run with 300 ppm each of benzene and toluene is taken for representing the general trend in variation of total flux with time for all the experimental runs. A sudden drop in flux and selectivity can be observed in the first hour. This may be due the fact that the membrane might be swollen. It is believed that by definition the pervaporation membrane is viewed as a stack of thin films once the permeating components have made the membrane totally wet. At this complete wet stage the

membrane is considered to be swollen membrane. This condition is achieved, in general terms, with in two to three hours of the operation. Indeed, such understanding and explanation is clearly evident from Fig. 5.5 and Fig. 5.6. Obviously, once the membrane gets totally wet and the downstream side is kept dry, steady state phenomenon may be observed. The sorption on the liquid side produces a substantial swelling of the membrane matrix. This anisotropic swelling is a characteristic feature of pervaporation. Therefore, as the membrane is viewed as stack of thin films (where the interactions between polymers and penetrants take place) the situation may lead to nonlinear expressions for solubility and diffusivity. Further, higher solubility's of benzene and toluene (compared to water) may also be the possible reason for the higher values of selectivity's. However, after some time, once both the components become soluble in the membrane (up to an equilibrium level) the diffusivity may then play a decisive role for drop in selectivity. Moreover, coupling and concentration polarization come into the effect and finally the values reach a steady state from this uncertain region.

Experiments were carried out at different Benzene and Toluene composition as given Table 5.2, maintaining the total organic content in the medium 600 ppm. It may be noted that the total organic load on the membrane remains the same. Only the compositions of Benzene and Toluene are changed. Fig. 5.6 shows the selectivity variation with time for the 300-300ppm Benzene - Toluene run. From the figure it is proved, as being stated earlier, that the membrane shows greater affinity towards benzene than toluene as both are having equal concentrations in the feed.

Table 5.2: Concentration of benzene and toluene for 600 ppm total organics

(* Toluene concentration out of solubility limit)

Experimental Run Number	Benzene Concentration (ppm)	Toluene Concentration (ppm)
1	600	0
2	450	150
3	300	300
4	150	450
5	0	600*

Total Flux Vs Time.
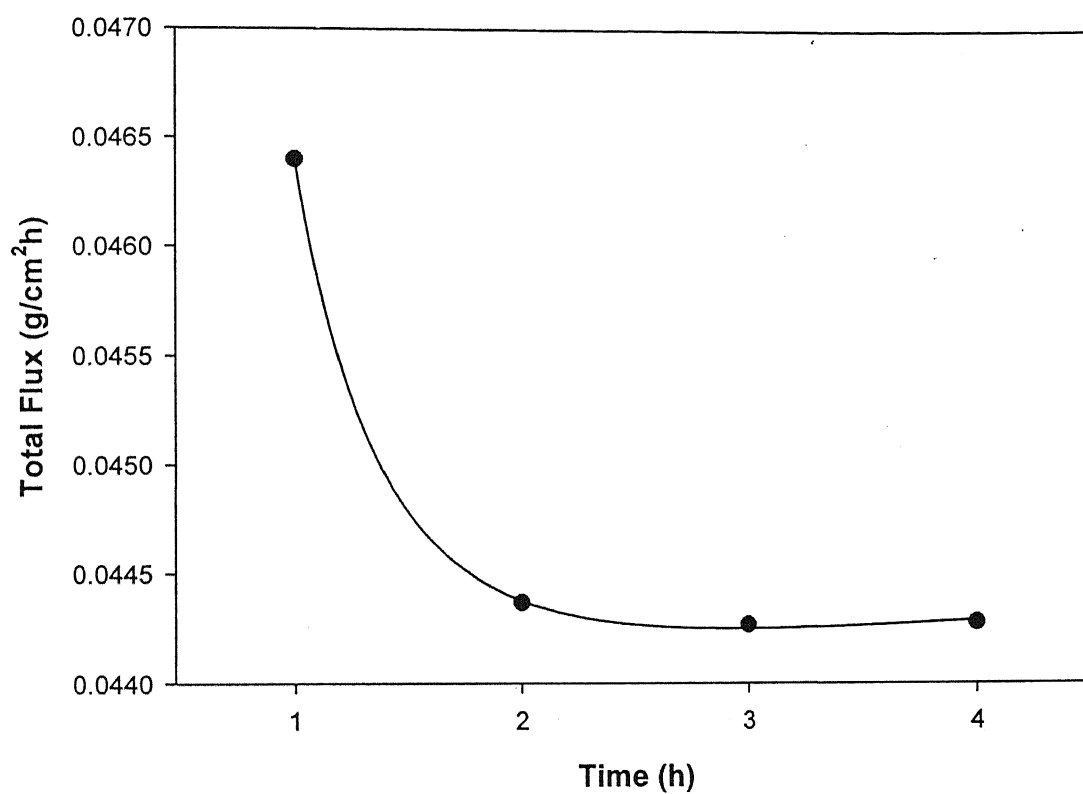
Fig 5.5: Variation of total flux with time for 300-300 ppm benzene-toluene feed
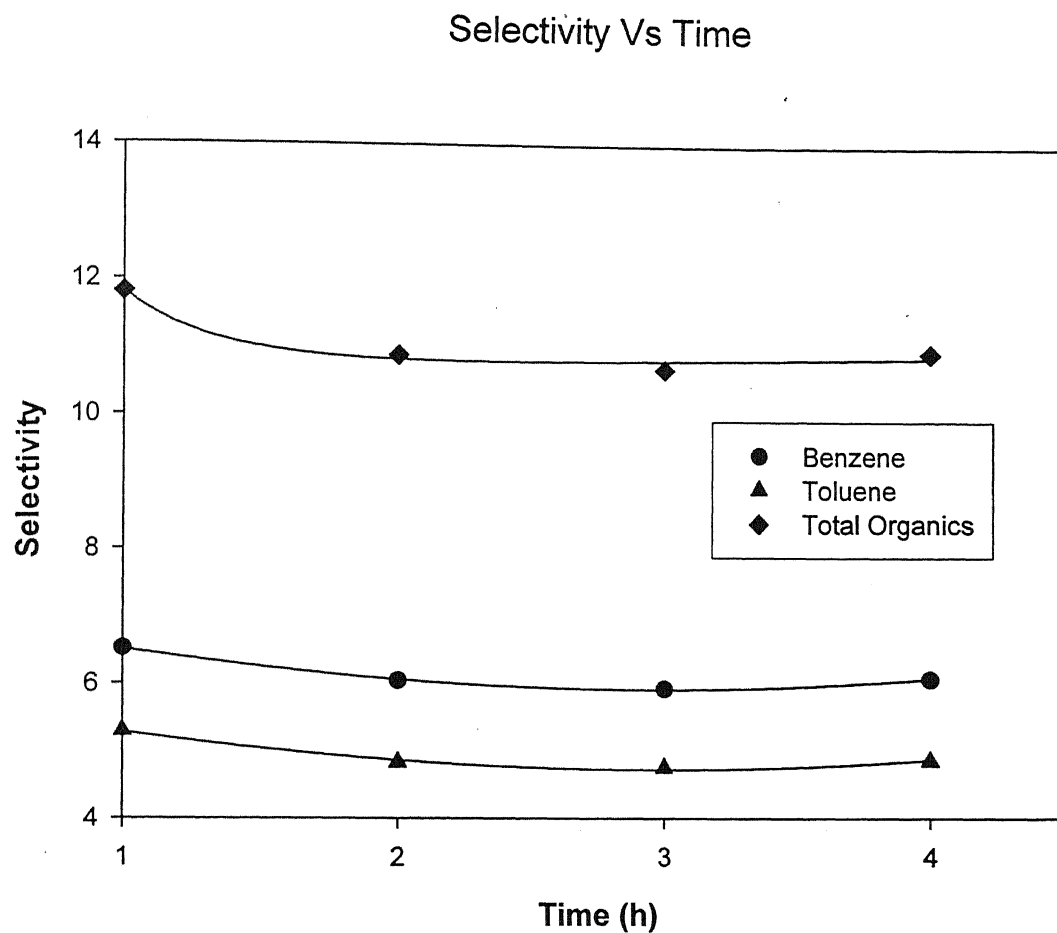
Selectivity Vs Time

Fig 5.6: Selectivity vs. time for 300-300 ppm benzene-toluene feed

All the experiments were carried out with in the solubility range of benzene and toluene (with one exception - the solubility of toluene in water is 500 ppm at 20°C & toluene concentration was taken 600 ppm). Outside solubility range (marginal) solution may be considered to be homogeneous under well dispersed phase of toluene in water.

It has been already observed and explained that one may achieve higher selectivity for organics in the presence of more than one component due to the effect of coupling. Fig. 5.7 shows a similar trend to that of Fig 5.1. The maximum selectivity obtained for the organics with 400 ppm was 8.61; but, for 600 ppm, the maximum selectivity increased to 10.83. This is an expected result. This may be explained because of the fact that as the concentration of the component increases the solubility of that component also increases. This, in turn, increases the selectivity. Further, there is always an inverse relationship with flux and selectivity. This results in drop in flux with increase in selectivity with increase in concentration of organic. Therefore, the flux comes to a minimum (as shown in Fig 5.8 - a similar nature to Fig 5.2) with highest value of obtained selectivity. Obviously, the flux for 600 ppm concentration organics will be higher than that for 400 ppm concentration (because of the solubility effect). Further, Fig 5.9 depicts such inverse relationship between selectivity and total flux (obviously under similar total organic concentration in the feed).

There may be a basic difference between the single component VOC system and a multi-component VOC system. In the single component system, the separation parameter is the selectivity of the membrane (only) which gives the measure of selectivity of the VOC with respect to the water. But in the case of multi component aqueous system there is a separation of each of the VOC components with respect to water as well as also with respect to each other (defined as separation factor). Thus, the separation factor is the measure of how much the membrane is selective between organic components. Fig. 5.10 shows the variation of toluene separation factor as a function of benzene percent in organics. It is found that at a higher toluene concentration in the feed there is higher toluene flux compared to benzene flux. Similarly, with an increase in benzene concentration (in the feed) the membrane preferentially passes benzene in comparison to toluene. The separation factor of toluene is less than one in presence of equal amounts of benzene and toluene. This shows the membrane to be more selective to benzene.

Total Selectivity Vs Benzene % in Organics

Fig 5.7: Variation in total selectivity with benzene concentration for 600 ppm organic concentration

Flux Vs Benzene % in Organics

Fig 5.8: Variation in total flux with benzene concentration for 600 ppm organic concentration
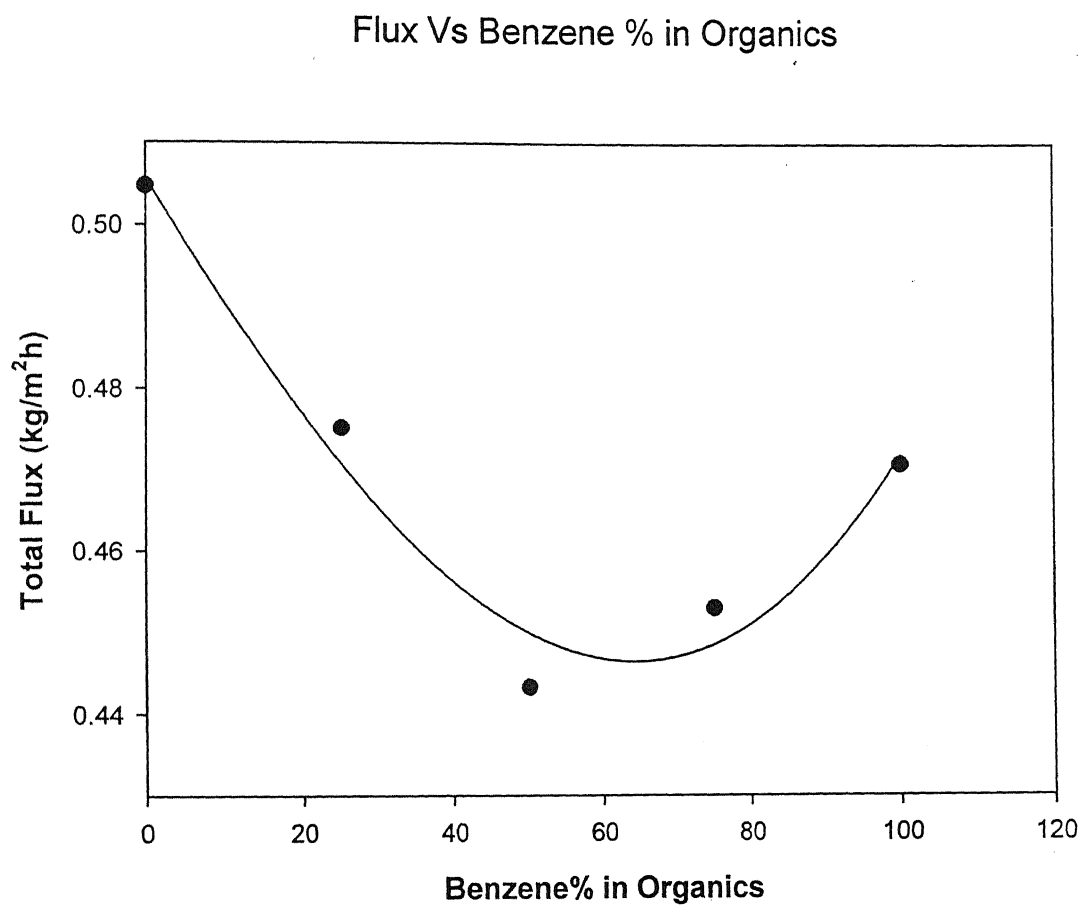
Total Flux Vs Total Selectivity

Fig 5.9: Relationship between total flux and selectivity for 600 ppm organic concentration

Toluene Separation Factor Vs Benzene % in Organics

Fig 5.10: Variation in toluene separation factor with benzene concentration for 600 ppm organic concentration

Selectivity Vs Toluene, Benzene % in Organics
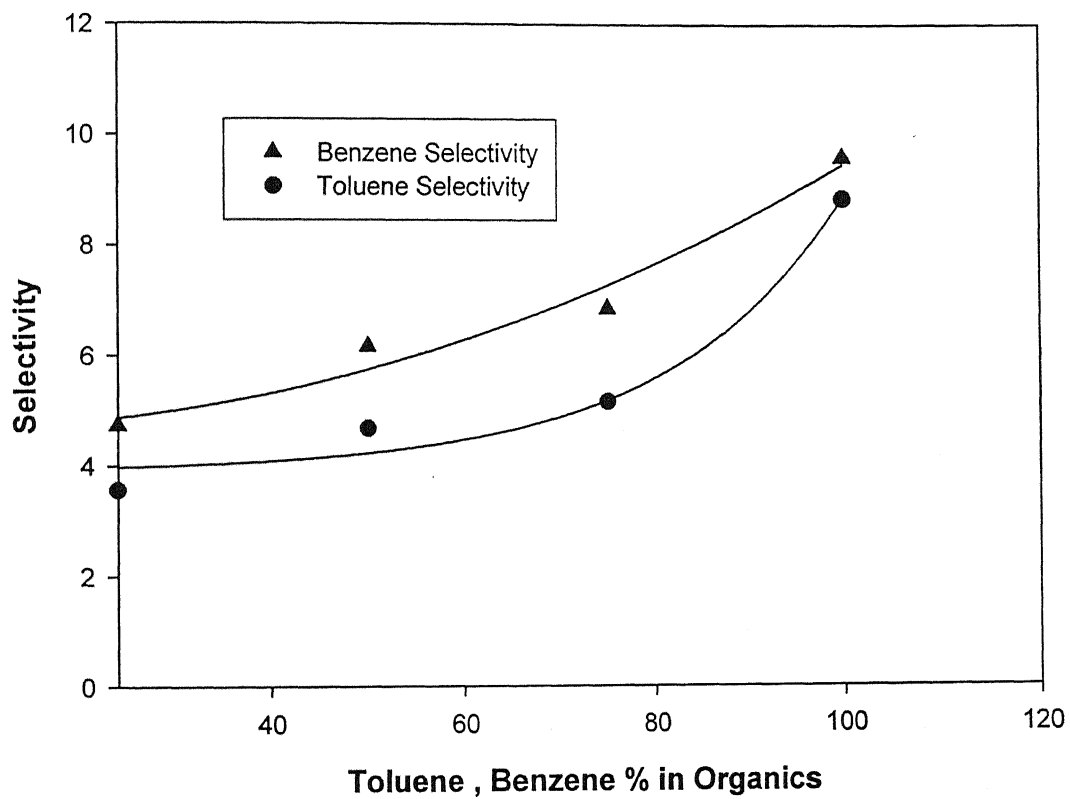
Fig 5.11: Variation of partial selectivity with partial organic concentration for 600 ppm organic concentration

Fig. 5.11 compares the selectivity of benzene and toluene with change in their compositions in the feed. It is observed that there is an increase in selectivity of benzene and toluene with corresponding increase in their compositions. Initially, it may be observed that the selectivity of benzene increases but with smaller increment with composition and then finally with higher compositions the selectivity attains sharp increase. This observation may be explained through the concept of sharing of driving forces by these two organic compounds. If the composition is such that one of the compounds is dominating then the sharing of driving force decreases in that proportion. Thus, once toluene concentration is much higher than benzene (for e.g. toluene/benzene – 80/20), the driving force for toluene shared by benzene is also less. Hence, the selectivity increases much more compared to its lower concentration. The explanation can similarly be written for benzene as well. Accordingly, higher concentrations of each of these organic compounds are showing much higher rises of selectivity's. In order to explicitly explain the results obtained for toluene concentration beyond its solubility limit (for the present case - 600 ppm) it may be mentioned that the binary solution of toluene in water was considered homogenous (although in reality it is highly dispersed which may be a close condition for homogeneity). Indeed results also depict according to assumption. Above results may also be compared with the results obtained for 400 ppm of total organics as was shown in Fig. 5.4. There also a sudden increase in selectivity is observed.

5.3 Total organic concentration: 800 ppm

A feed mixture containing 800 ppm of total organics i.e. benzene and toluene in aqueous medium was used with PERVATECH Teflon coated composite Poly-Dimethyl Siloxane (PDMS) as PV membrane at a temperature of 30°C. Experiment was continued until pseudo steady state flux was obtained. Permeate concentrations were analyzed and the results are discussed below.

Experiments were carried out at different benzene and toluene composition as given Table 5.3, maintaining the total organic content in the medium 800 ppm. Fig. 5.12 shows the total organic selectivity variation with change in benzene concentration in the organics. It may be noted that although a maxima is observed (Fig. 5.12) but such maximum value is towards higher benzene concentration. This kind of results was more
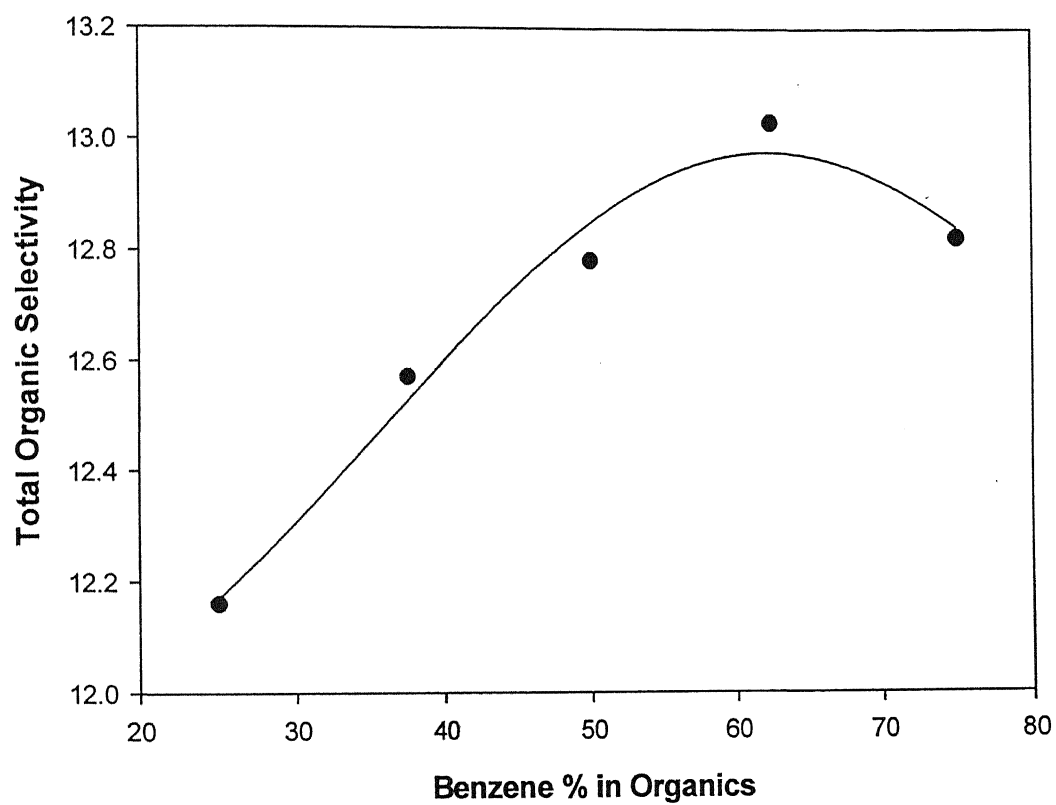
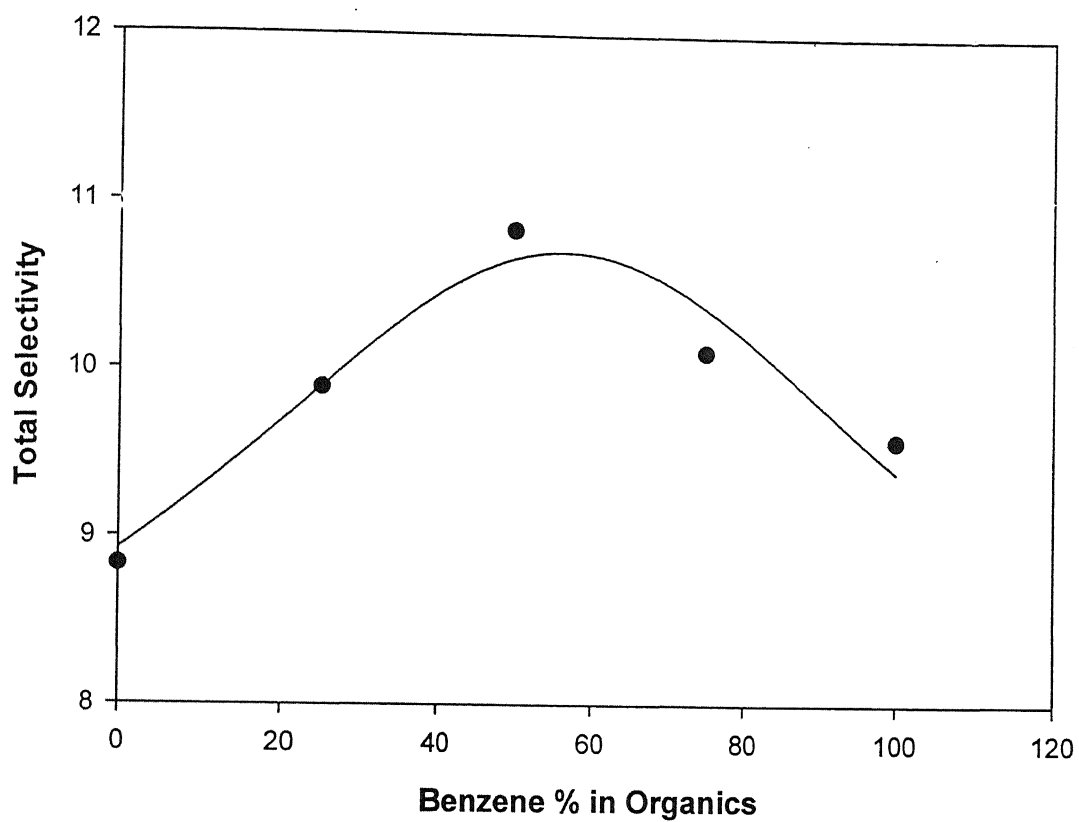Fig 5.12: Total organic selectivity variation with benzene concentration for 800 ppm organic concentration
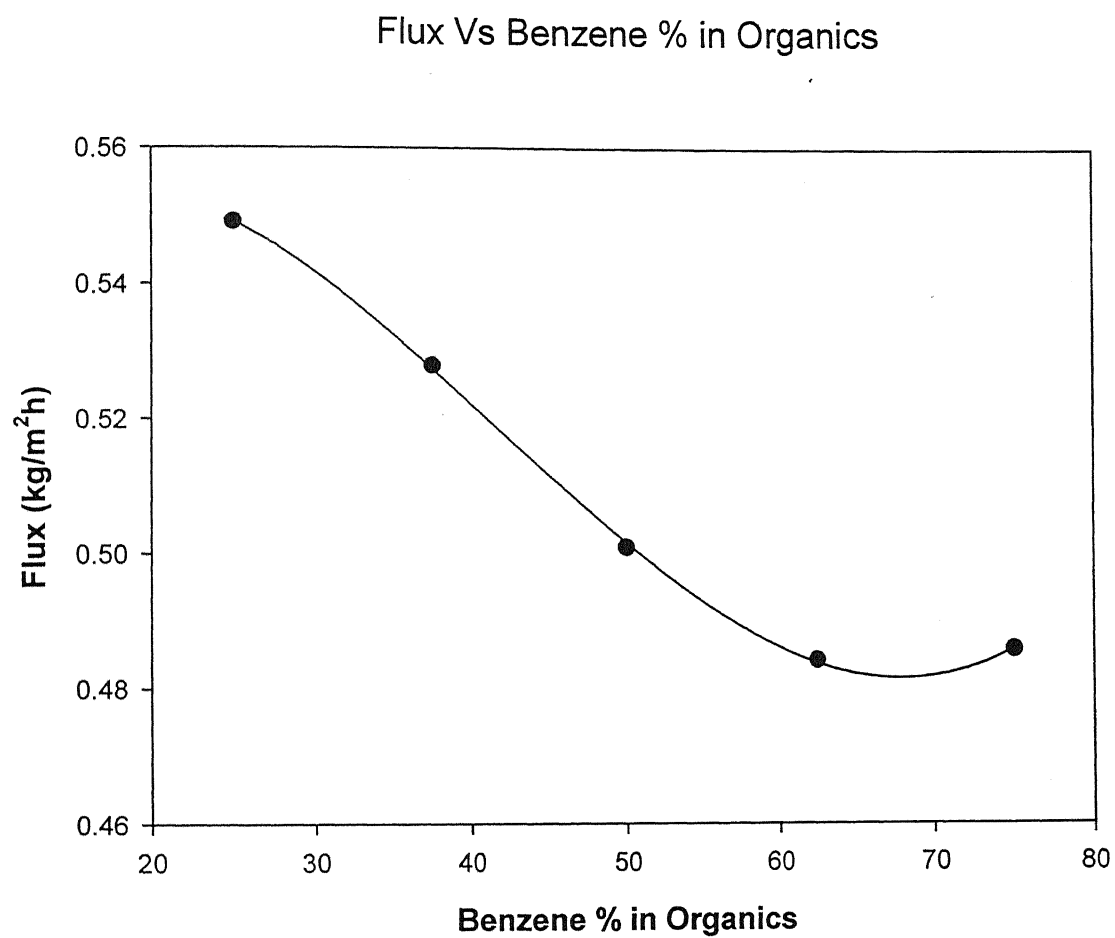
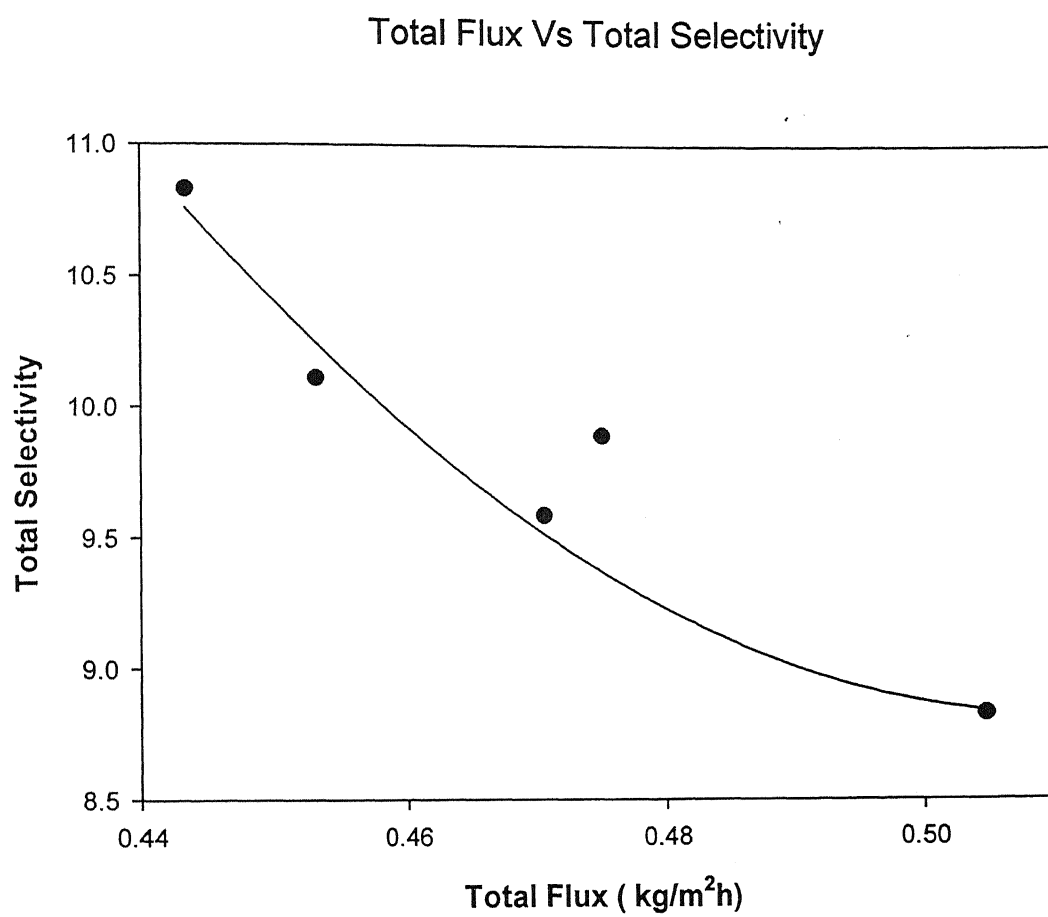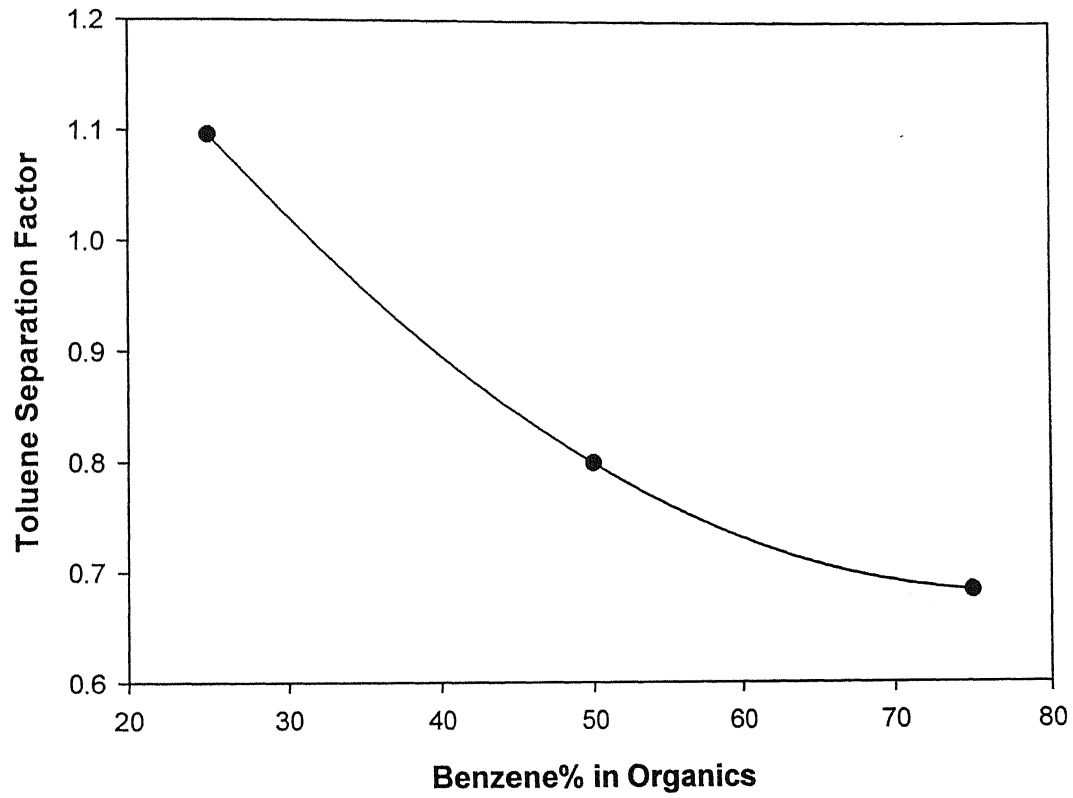Fig 5.13: Variation in total flux with benzene concentration for 800 ppm organic concentration

Fig 5.14: Variation in benzene separation factor with benzene concentration for 800 ppm organic concentration
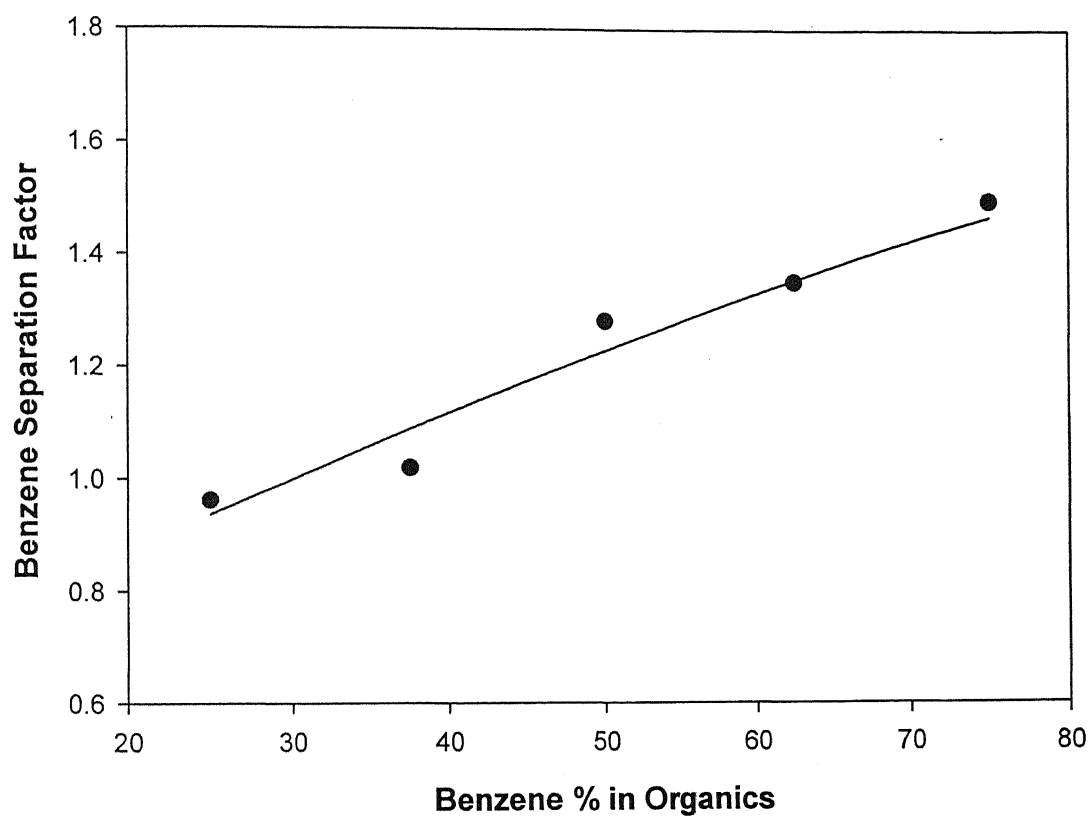
Total Flux Vs Total Organic Selectivity
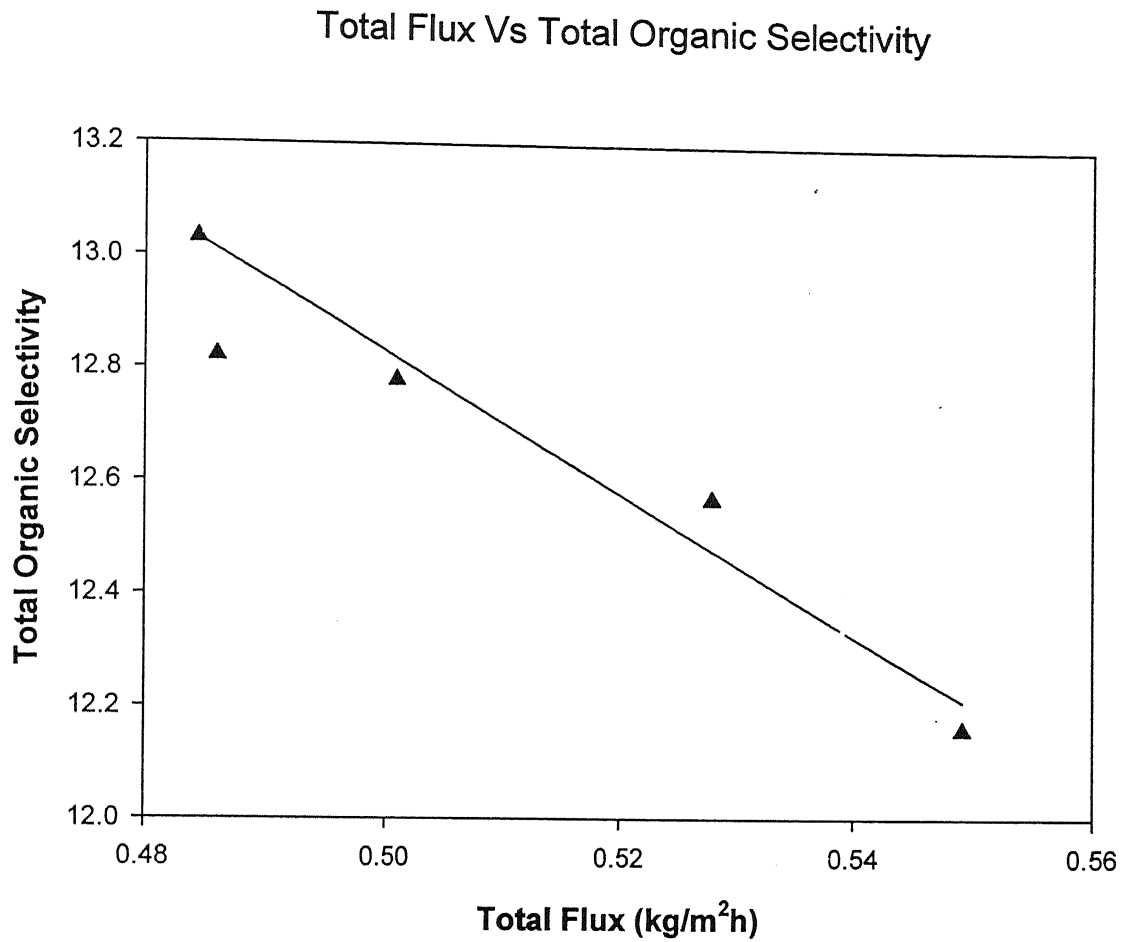
Fig 5.15: Relationship between total flux and selectivity for 800 ppm total organic concentration

Benzene,Toluene Selectivity Vs Benzene % in Organics
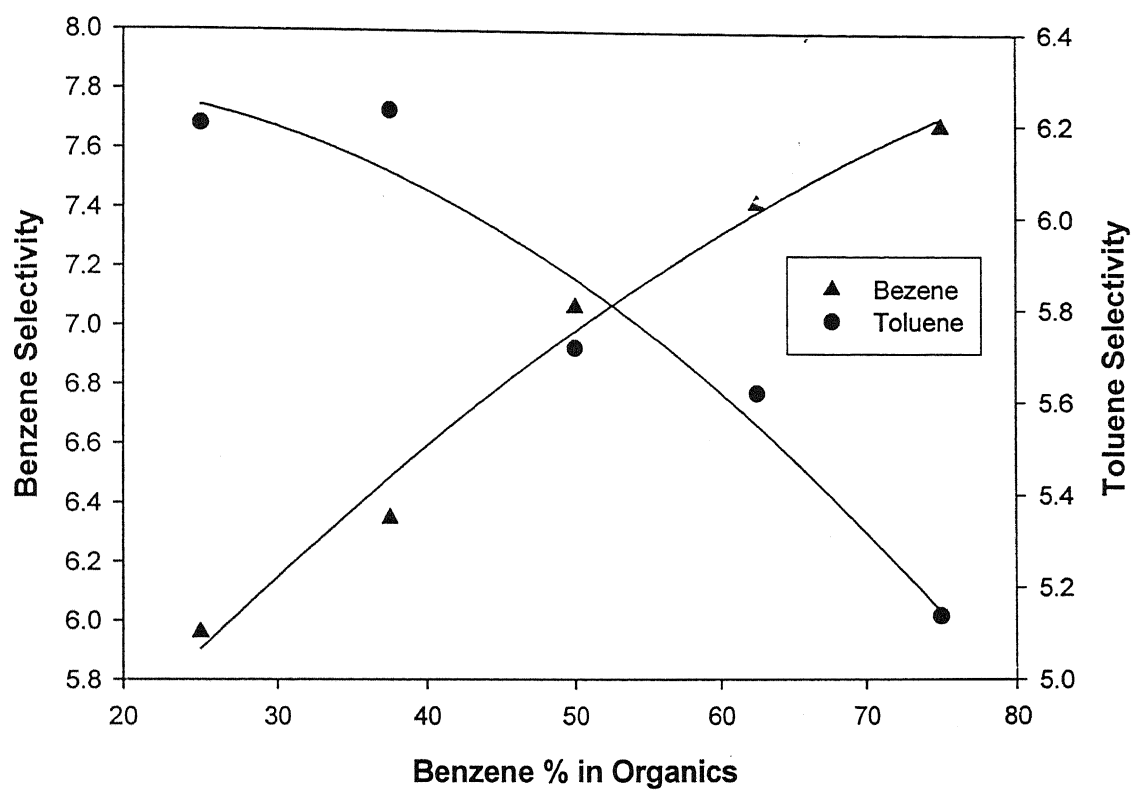
Fig 5.16: Relationship between benzene and toluene selectivity to benzene % in organics for 800 ppm organic concentration

It is clear from the Fig. 5.16 that there is a decrease in toluene selectivity with increase in benzene concentration and a corresponding increase in benzene selectivity. This explains the increase in benzene separation factor or decrease in toluene separation factor, as may also be observed from Fig 5.3, Fig 5.10 and 5.14.

5.4 Equal amounts of benzene and toluene in aqueous medium

In the first three sets of experiments, the total organic concentrations were kept constant and the component concentrations were changed. In this set of experiments, benzene and toluene were taken in equal amounts; however, at different total organic concentrations. Experimental conditions are given in Table 5.4.

Table 5.4: Concentration of benzene and toluene in equal amounts

Experimental Run Number	Benzene Concentration (ppm)	Toluene Concentration (ppm)
1	200	200
2	300	300
3	400	400
4	500	500

A feed mixture containing equal amounts of benzene and toluene was used with PERVATECH Teflon coated composite Poly-Dimethyl Siloxane (PDMS) as membrane at a temperature of 30°C. Experiment was continued until pseudo steady state flux was obtained. Permeate concentrations were analyzed and the results are discussed below.

Fig 5.18 shows the variation in total flux with increase in organic concentration in the feed. It is found that there is an increase in flux with increase in organic concentration and that the change is linear. In all of the earlier sets of experiments, it was observed that flux declined with increase in benzene concentration (due to higher selectivity of

benzene) as the organic load on the membrane was kept constant. However, in the present set of experiment, the ratio of benzene to that of toluene is 1:1. Therefore, the flux increases with increase in organic load (as the membrane is organophilic) only.

Fig. 5.17 shows the change in selectivity of membrane with variation in concentration of organics in feed. It is found that the selectivity of the membrane increases with increase in concentration of organics. This result is in sharp contrast with the results obtained in earlier sets where flux and selectivity was found to have an inverse relationship. This variation in relationship is attributed to the increase in total organics (constant in the earlier set of runs).

Fig. 5.19 gives a clearer picture of the selectivity of benzene and toluene. It can be seen that there is greater difference in the selectivity between the two components at higher organic concentrations even though they are present in the ratio 1:1. This result also helps to understand the shift in the maxima of total organic selectivity towards higher benzene concentration, as shown in Fig 5.1, Fig 5.7 and Fig 5.11. Referring Fig. 5.19, it is clear that even at 1:1 concentration (benzene - toluene) the membrane is more selective to benzene with increase in total organic concentration. Whereas, in the case of other than 1:1 concentration, the maxima shifts towards higher benzene concentration with increase in the total organic concentration (refer Fig 5.1, Fig 5.7 and Fig 5.11).

Fig 5.20 depicts the change in benzene separation factor with total organic concentration. As it is obvious, benzene separation factor increases with total organic concentration because at higher organic concentration benzene is more selective.

Total Organic Concentration Vs Total Flux
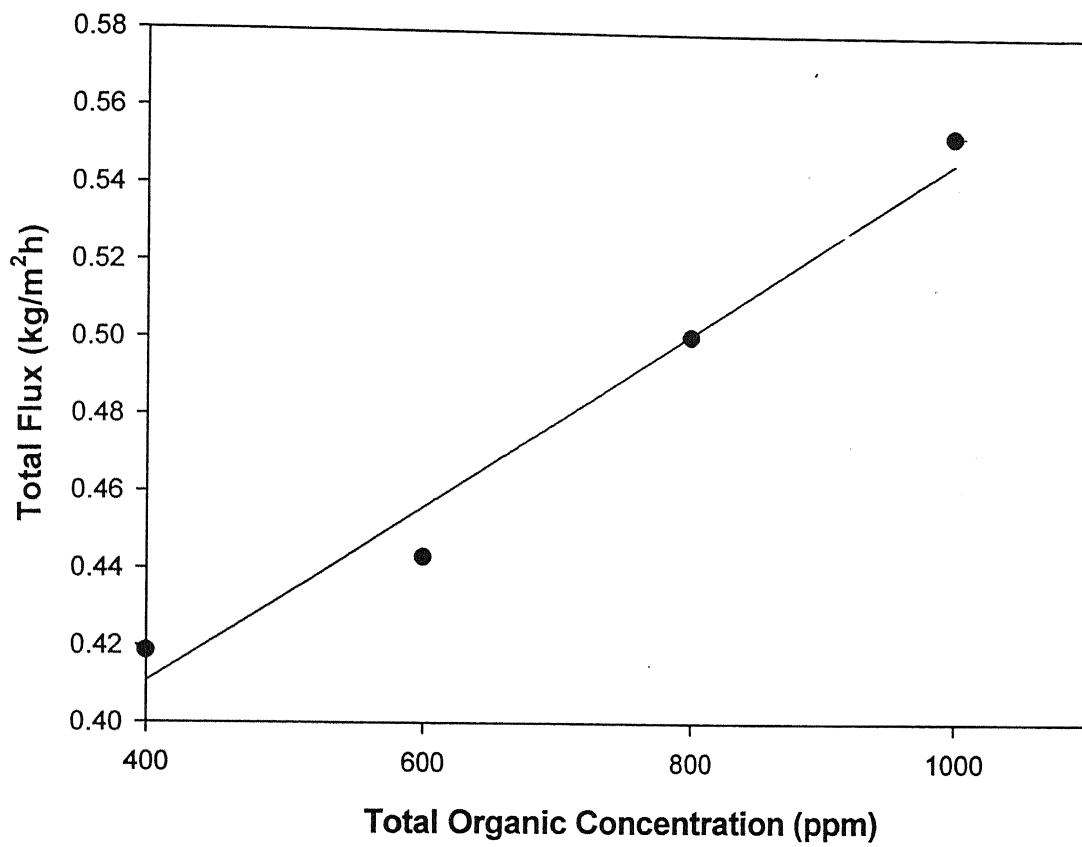
Fig 5.17: Variation in total flux with total organic concentration

Total Organic Concentration Vs Total Organic Selectivity
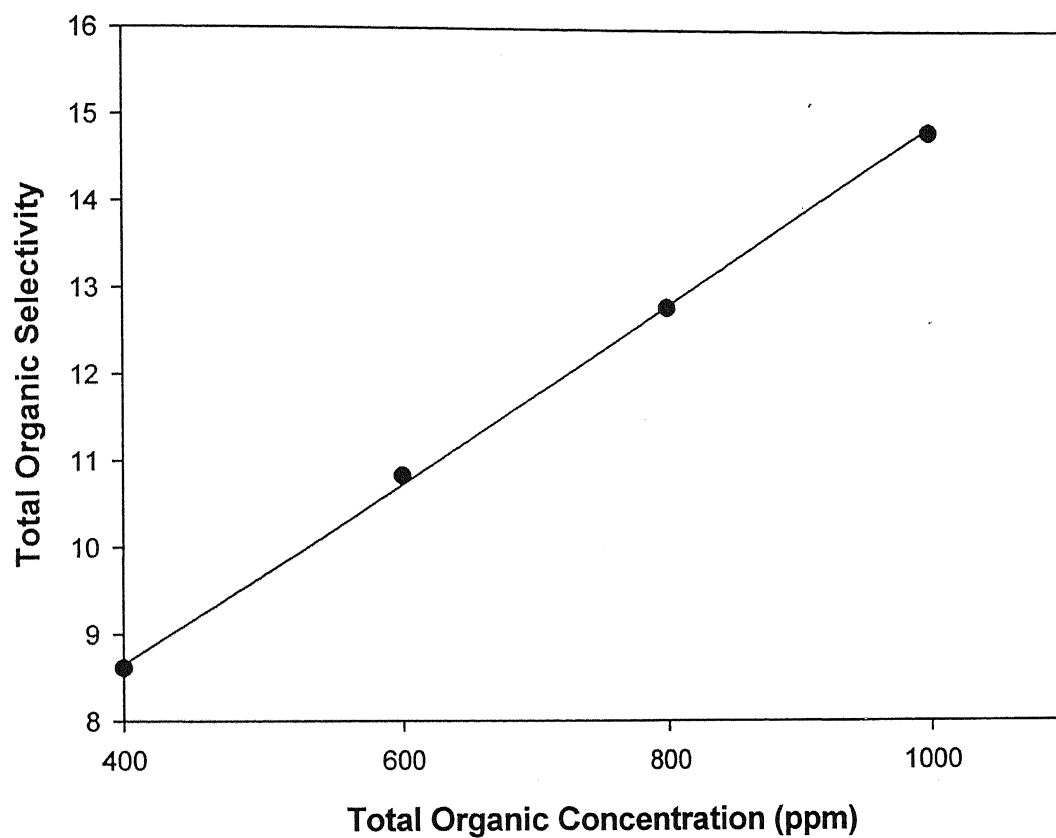
Figure 5.18: Variation in total organic selectivity with total organic concentration

Selectivity of VOCs Vs Total Organic Concentration
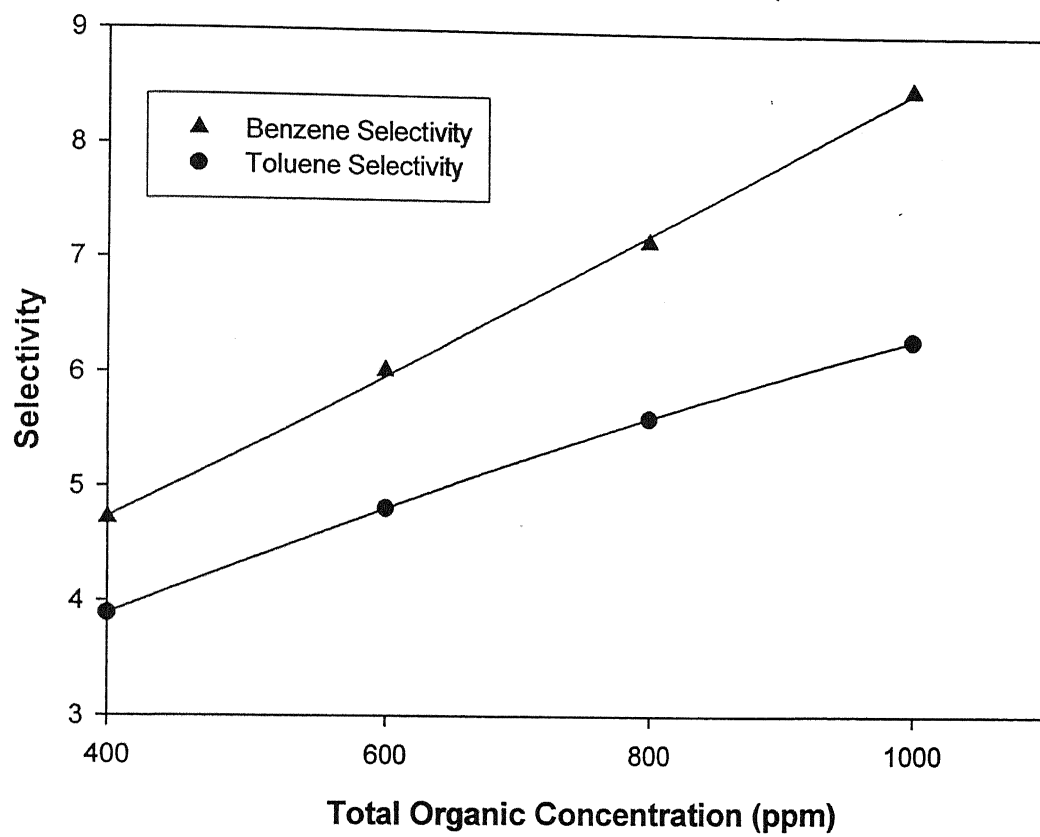
Figure 5.19: Variation in selectivity of benzene and toluene with total organic concentration

Total Organic Concetration Vs Benzene Separation Factor
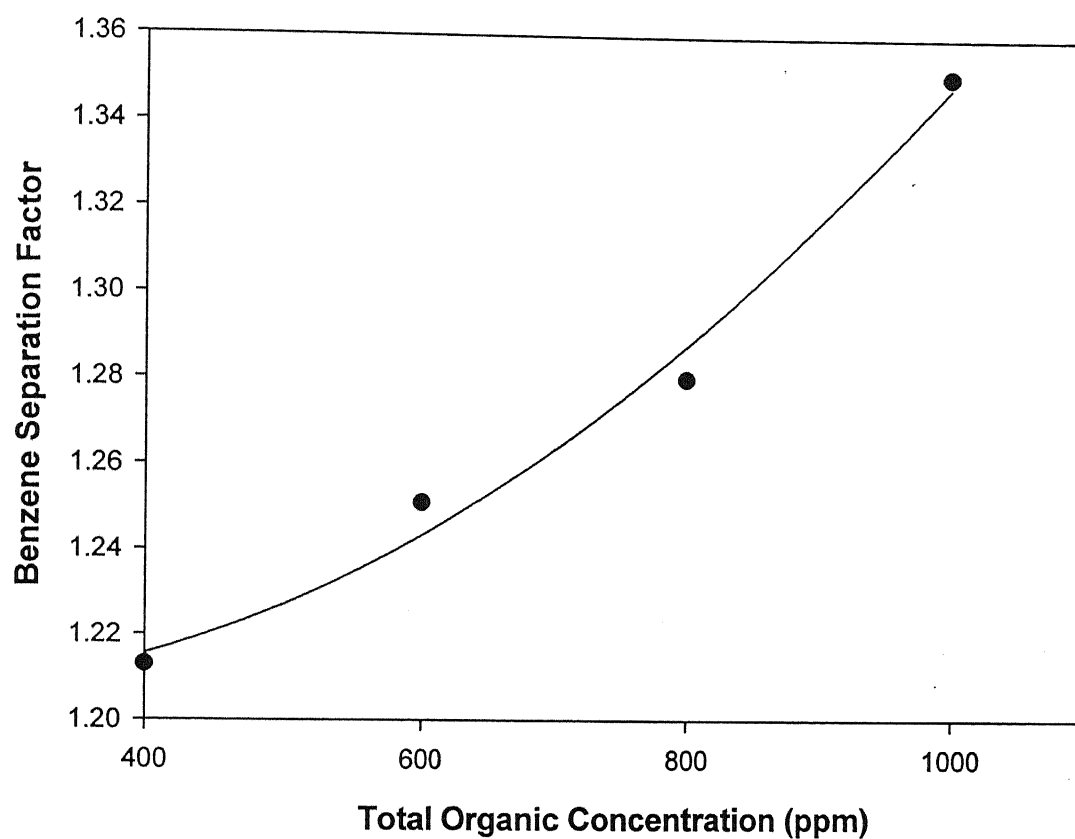
Figure 5.20: Variation in benzene separation factor with total organic concentration

5.5 Comparison of experimental data with model predicted data for Equal concentration of benzene and toluene in aqueous solution

Fig 5.21 depicts the change in total organic flux in permeate side with Total Organic concentration. As it is obvious, VOC flux increases with Total Organic concentration in feed and it is found that there is an increase in Flux with organic concentration and that the change is linear, this trend is shown with experimental and model predicted data. Similarly, Fig. 5.22 also shows the compatibility of this model with respect to water flux with increase in VOC concentration in feed.

Fig.5.23 shows the change in total organic selectivity of membrane with variation in concentration of organics in feed. It is found that the selectivity of the membrane also increases with increase in concentration of organics. With an increase in organics in the feed, the membrane being selective to the organics shows greater selectivity as got experimentally as well as by model also.

For dilute solution, the selectivity at a point may be defined on a mass basis as

$$\text{Selectivity} = \frac{J_A M_A}{J_B M_B} \left(\frac{\rho - C_{AL} M_A}{C_{AL} M_A} \right) \approx \frac{J_A \rho}{J_B M_B C_{AL}} \tag{5.1}$$

where

M_i = Molecular weight of component i

ρ = density of feed solution, kg/m^3

VOC flux Vs. VOC conc. in feed
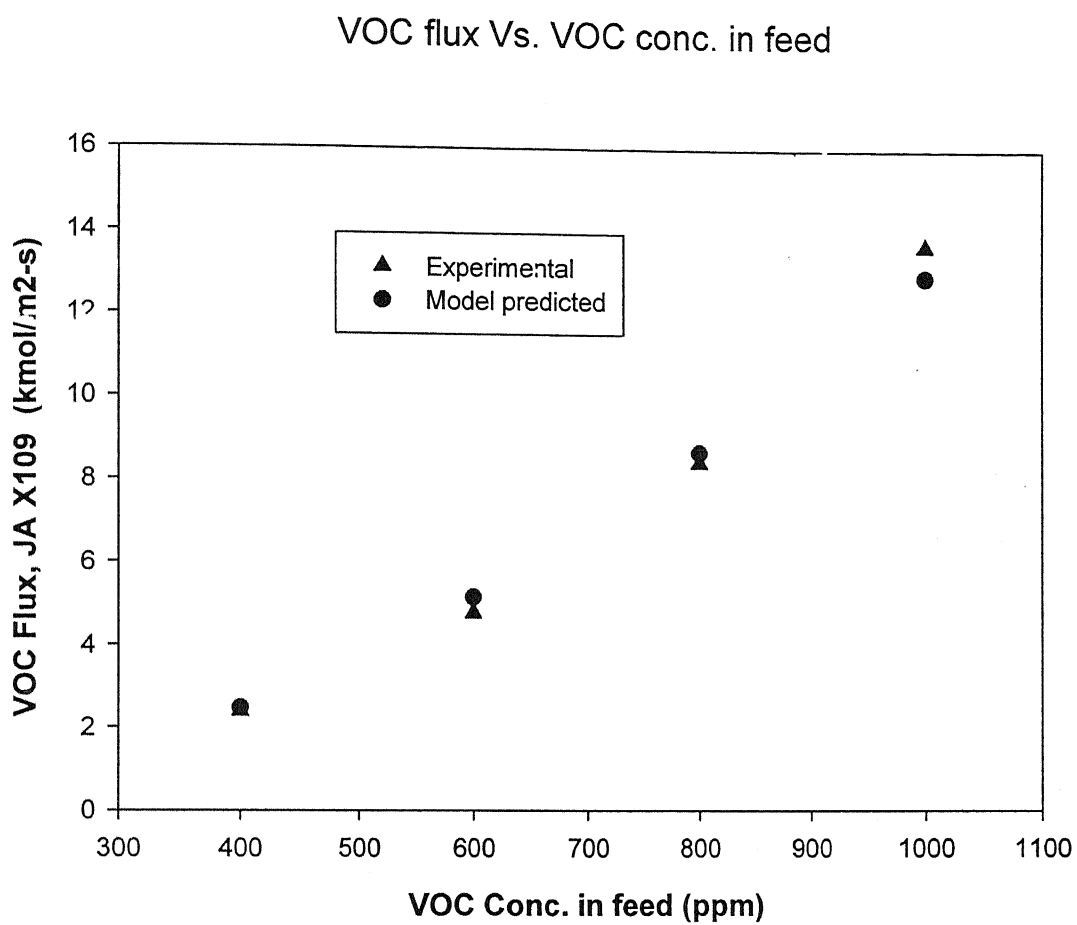
Fig 5.21: Variation in organic flux in permeate with Total Organic concentration (VOC) in feed

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Water flux Vs. VOC conc. in feed
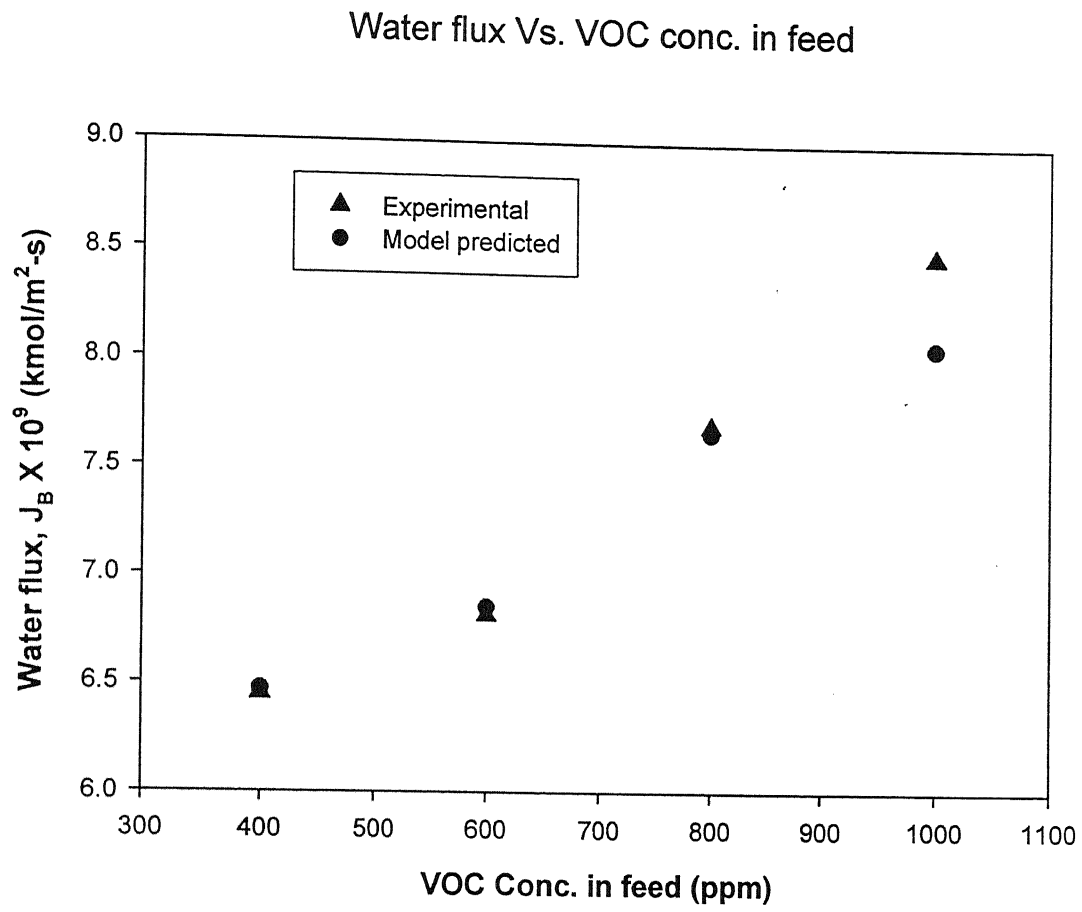
Fig 5.22: Variation in water flux in permeate side with Total Organic concentration (VOC) in feed

Total Organic selectivity in permeate Vs. VOC conc. in feed
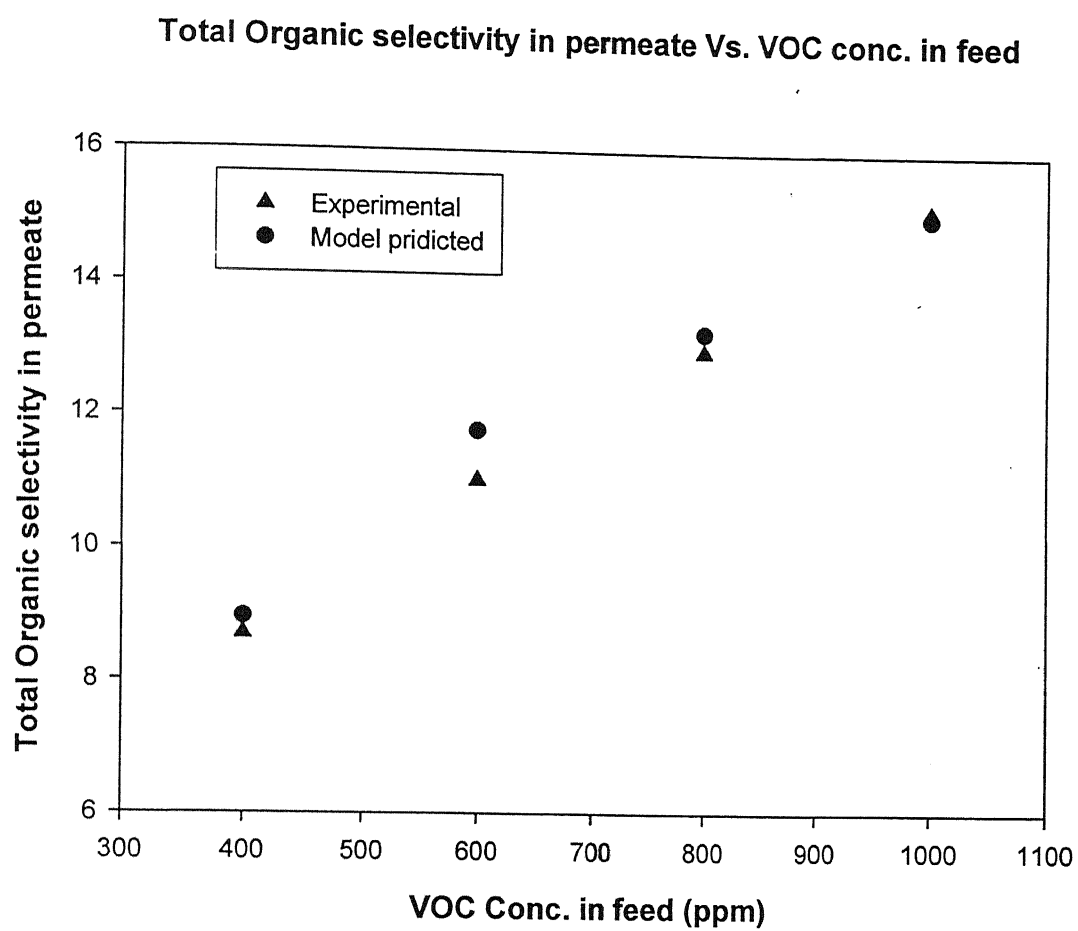
Fig 5.23: Variation in organic selectivity in permeate side with Total Organic
concentration (VOC) in feed

Based on the results and discussions of separation of multi component VOCs in aqueous solution pervaporation studies, following conclusions may be drawn:

i. Observations of flux and selectivity behaviour of constant Total Organic concentration in feed during pervaporation with respect to feed concentration show that an inverse relationship exits between these quantities.

ii. A maxima was obtained for the Total Organic Selectivity with change in Benzene % in Organics. This is attributed to the coupling effect in the case of muti component mixtures.

iii. The maxima in Total Organic selectivity with change in Benzene concentration at constant Total Organic concentration shifts towards the higher Benzene concentration side, with increase in Total Organic concentration. This is because membrane is more selective to Benzene than Toluene and with increase in Total Organic concentration the maxima shifts towards the higher Benzene concentration side.

iv. Coupling Effect is an important phenomenon in the multi component systems where there is competitive transfer of more than one preferential component.

v. .The selectivity of the organophillic PDMS membrane is greater when more than one organics is present in the feed compared to that when there is only one organic compound in the feed. This is due to coupling effect due to which the driving force on one component may affect the transfer of the other component.

vi. Observations of flux and selectivity behavior at differing Total Organic concentration in feed during pervaporation with equal Benzene – Toluene concentration show that both the quantities increase with increase in organic concentration in the feed.

vii. With increase in Total Organic concentration the membrane has greater selectivity for Benzene even when the concentration of Benzene and Toluene in the feed is the same.

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viii.The experimental values obtained for total organic selectivity and organic and water fluxes of equal concentrations of benzene and toluene in aquous solution matches well with model predicted values.

CHAPTER 7

RECOMMENDATIONS

Based on the work carried out for the separation of multi component VOCs in aqueous solution by pervaporation, several experiences were gained, some of which are listed below as recommendations for future work.

i. Further investigations can be done with multi component VOCs by changing other parameters such as permeate side pressure, temperature, feed flow rate etc.

ii. Any experimental work is niot complete until a model predicting the flux and selectivity is obtained. Modeling for pervaporative separation of Multi Component system is recommended.

iii. Use of laboratory cast dense membranes instead of commercial ones may avoid the uncertainty in the properties used in this model. Also organophilic and organoselective membranes may be used for verifications of the model.

iv. Studies can further be extended with three organic compounds, which will be a more practical case..

v. Finally VOCs as the name suggest is highly volatile and should be handled with care to get accurate concentrations. So an online measurement of the permeate is the best option to reduce errors.

vi. A model developed for predicting the flux and selectivity values for constant total organics in the feed with varying composition of components.

Appendix A

A1: Toluene - Water Calibration Curve*

(* *In the presence of Benzene*)

Reference Compound: Phenol

Phenol concentration: 100ppm

Table A1.1: Calibration curve data for toluene – water system

Toluene (ppm)	Toluene/Phenol Area Ratio
118	0.6018
149	0.7547
181	0.8923
212	1.0251
242	1.1770
297	1.3301
352	1.5341
404	1.8741

Toluene - Water Calibration Curve
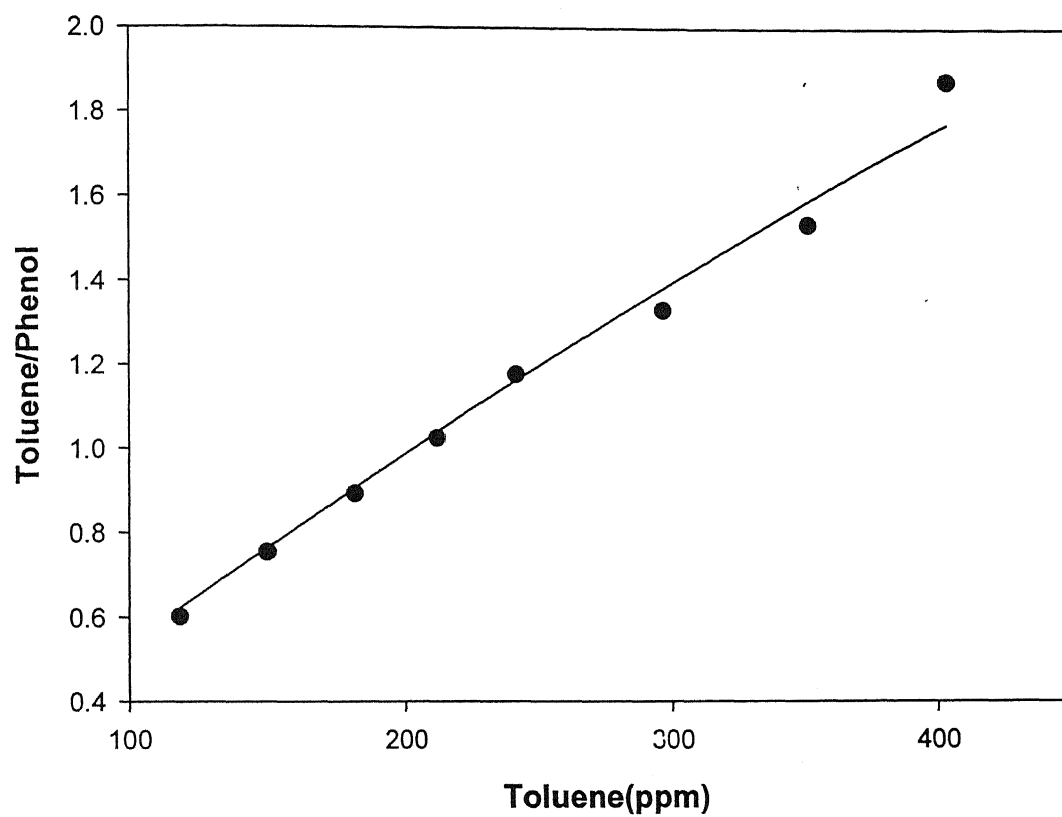
Fig A1.1: Toluene – Water Calibration Curve

A2: Benzene - Water Calibration Curve*

(* *In the presence of Toluene*)

Reference Compound: Phenol

Phenol concentration: 100ppm

Table A2.1: Calibration curve data for benzene – water system

Benzene (ppm)	Benzene/Phenol Area Ratio
104	0.5944
152	0.8119
200	1.069
250	1.495
296	1.752
347	2.057
395	2.380
446	2.790

Benzene - Water Calibration Curve
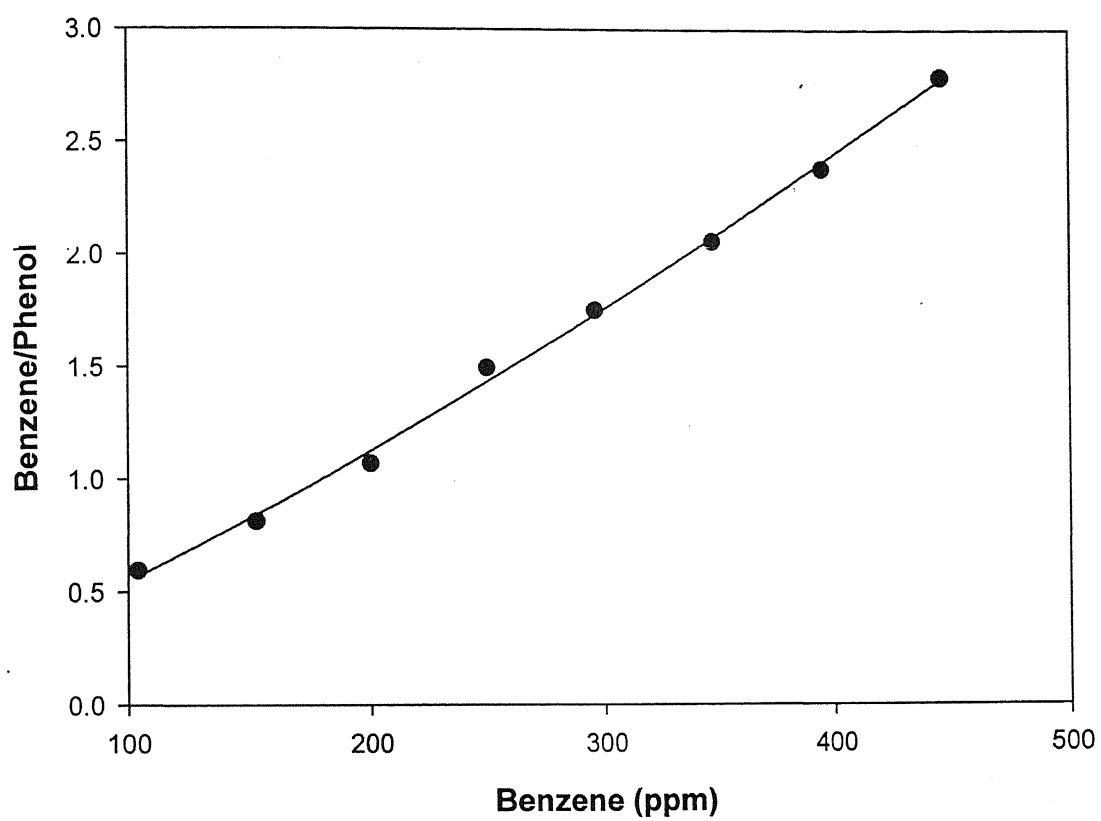
Fig A2.1: Benzene – Water Calibration Curve

Appendix B

System: 400 ppm total organics

Membrane: PERVAP Teflon coated PDMS
Feed: water - benzene - toluene
Temperature: 30°C
Downstream Pressure: 2 mm Hg

B1: Variation of selectivity with benzene % in organics

Experimental Run Number	Benzene % in Organics	Total Selectivity
1	0	8.100
2	25	8.410
3	50	8.610
4	75	8.490
5	100	8.230

B2: Variation of total flux with benzene % in organics

Experimental Run Number	Benzene % in Organics	Total Flux (kg/m^2h)
1	0	0.4316
2	25	0.4250
3	50	0.4186
4	75	0.4197
5	100	0.4221

B3: Variation of benzene separation factor with benzene % in organics

Experimental Run Number	Benzene % in Organics	Benzene Separation Factor
1	0	-
2	25	0.905
3	50	1.202
4	75	1.370
5	100	-

B4: Variation of toluene selectivity with toluene % in organics

Experimental Run Number	Toluene % in Organics	Toluene Selectivity
1	0	-
2	25	3.510
3	50	3.910
4	75	4.320
5	100	8.100

Appendix C

System: 600 ppm total organics

Membrane: PERVAP Teflon coated PDMS
Feed: water - benzene - toluene
Temperature: 30°C
Downstream Pressure: 2 mm Hg

C1: Variation of total flux with time for 300-300 ppm benzene-toluene feed

Experimental Run Number	Time (h)	Total Flux (g/m^{2}h)
1	1	0.0464
2	2	0.04437
3	3	0.04427
4	4	0.04428

C2: Selectivity vs. time for 300-300 ppm benzene-toluene feed

Time (h)	Benzene Selectivity	Toluene Selectivity	Total Selectivity
1	6.52	5.29	11.81
2	6.01	4.87	10.88
3	5.99	4.69	10.68
4	6.07	4.87	10.94

C3: Variation of selectivity with benzene % in organics

Experimental Run Number	Benzene % in Organics	Total Selectivity
1	0	8.830
2	25	9.890
3	50	10.830
4	75	10.110
5	100	9.587

C4: Variation in total flux with benzene concentration

Experimental Run Number	Benzene % in Organics	Total Flux (kg/m^2h)
1	0	0.5047
2	25	0.4751
3	50	0.4433
4	75	0.4530
5	100	0.4706

C5: Relationship between total flux and selectivity

Experimental Run Number	Total Flux (kg/m^{2}h)	Total Selectivity
1	0.5047	8.830
2	0.4751	9.890
3	0.4433	10.830
4	0.4530	10.110
5	0.4706	9.587

C6: Variation in toluene separation factor with benzene concentration in organics

Experimental Run Number	Benzene % in Organics	Toluene Separation Factor
1	0	-
2	25	1.0961
3	50	0.7994
4	75	0.6840
5	100	-

C7: Variation of partial selectivity with partial organic concentration

Benzene % in Organics	Toluene % in Organics	Benzene Selectivity	Toluene Selectivity
0	100	-	8.830
25	75	4.718	5.172
50	50	6.020	4.810
75	25	6.004	4.106
100	0	9.587	-

Appendix D

System: 800 ppm total organics

Membrane: PERVAP Teflon coated PDMS
Feed: water - benzene - toluene
Temperature: 30°C
Downstream Pressure: 2 mm Hg

D1: Total organic selectivity variation with benzene concentration

Experimental Run Number	Benzene % in Organics	Total Selectivity
1	25	12.160
2	37.5	12.570
3	50	12.780
4	62.5	13.030
5	75	12.821

D2: Variation in total flux with benzene concentration

Experimental Run Number	Benzene % in Organics	Total Flux (kg/m^2h)
1	25	0.5491
2	37.5	0.5279
3	50	0.5010
4	62.5	0.4843
5	75	0.4859

D3: Variation in benzene separation factor with benzene concentration

Experimental Run Number	Benzene % in Organics	Benzene Separation Factor
1	25	0.9617
2	37.5	1.0190
3	50	1.2800
4	62.5	1.3500
5	75	1.4950

D4: Relationship between total flux and selectivity

Experimental Run Number	Benzene % in Organics	Total Flux (kg/m²h)	Total Selectivity
1	25	0.9617	12.160
2	37.5	1.0190	12.570
3	50	1.2800	12.780
4	62.5	1.3500	13.030
5	75	1.4950	12.821

D5: Relationship between benzene and toluene selectivity to benzene % in organics

Benzene % in Organics	Benzene Selectivity	Toluene Selectivity
25	5.960	6.197
37.5	6.347	6.227
50	7.065	5.716
62.5	7.420	5.620
75	7.683	5.138

Appendix E

System: Equal amounts of benzene and toluene in aqueous medium

Membrane: PERVAP Teflon coated PDMS
Feed: water - benzene - toluene
Temperature: 30°C
Downstream Pressure: 2 mm Hg

E1: Variation in total flux with total organic concentration

Experimental Run Number	Total Organic Concentration (ppm)	Total Flux (kg/m²h)
1	400	0.4186
2	600	0.4431
3	800	0.5010
4	1000	0.5538

E2: Variation in total organic selectivity with total organic concentration

Experimental Run Number	Total Organic Concentration (ppm)	Total Selectivity
1	400	8.610
2	600	10.830
3	800	12.780
4	1000	14.821

E3: Variation in selectivity of benzene and toluene with total organic concentration

Total Organic Concentration (ppm)	Benzene Selectivity	Toluene Selectivity
400	4.717	3.890
600	6.020	4.813
800	7.165	5.615
1000	8.520	6.311

E4: Variation in benzene separation factor with total organic concentration

Experimental Run Number	Total Organic Concentration (ppm)	Benzene Separation Factor
1	400	1.213
2	600	1.251
3	800	1.280
4	1000	1.351

Appendix F

F1. Comparison of data predicted from model with experimental data:

Conc. Of VOC(ppm)	$J_A X 10^9$ (kmol/m^2-s) Experimental	$J_B X 10^6$ (kmol/m^2-s) Experimental	Selectivity (Experimental)	$J_A X 10^9$ (kmol/m^2-s) Model predicted	$J_B X 10^6$ (kmol/m^2-s) Model predicted	Selectivity Model predicted
400	2.386	6.449	8.691080	2.46535351	6.470522	8.950272
600	4.774	6.814	11.01858	5.14794894	6.85114	11.76729
800	8.499	7.692	12.97762	8.65049334	7.660831	13.26949
1000	13.656	8.482	15.13133	12.9063707	8.06083	15.044602

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